**PVD Processes for Depositing Hard Tribological Coatings**

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**Introduction**

Tribological coatings are those coatings that are applied to a component surface in order to control the friction and wear of that surface. In most cases, the goal is to reduce both the friction and wear, but there are instances such as in clutch components where a high coefficient of friction is a desirable property. Since this paper is being written to review advancements in tribological coatings as part of a series of papers commemorating the 50th anniversary of the Society of Vacuum Coaters, the content of this paper will concentrate on the coating technology for the deposition of thin, hard tribological coatings by physical vapor deposition (PVD) processes that take place in vacuum coating systems.

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**Initial PVD Hard Coatings Development**

Thin hard coatings of titanium carbide (TiC) on cemented carbide cuttings tools became available in the late 1960s, but these coatings were applied by atmospheric pressure chemical vapor deposition (CVD) processes. These first CVD hard coatings were very successful because they increased the life of the coated cutting tool by a factor of 4 or more.

In the early to mid 1970s, the coatings research community started looking at PVD techniques for depositing hard coatings. The CVD community did not think that much would come of this PVD work because the high temperature of the CVD process was required to produce an intermixed interfacial layer to promote good bonding. However, the high CVD deposition temperatures limited the application of the hard TiC coatings mainly to cemented carbide tooling.

One of the early pioneers in the field of PVD hard coatings was Professor Rointan F. Bunshah from UCLA. He and his coworkers developed a process called activated reactive evaporation (ARE) that was able to produce hard compound coatings with good adhesion to the substrate [1]. In this first paper, Bunshah and Raghuram reported on the high rate reactive deposition of compound coatings using oxygen, nitrogen, acetylene, or ammonia as the reactive gas, and they showed that a PVD process could be used to deposit hard tribological coatings. This early work by Bunshah gave hope to many others to pursue the deposition of thin, hard tribological coatings by PVD techniques.

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**Ion Plating**

The ARE process that Bunshah developed was really a variation of the ion plating process that had been discovered by Mattox [2-4]. Mattox showed that by creating a plasma around the substrate during deposition, it was possible to extract ions from this plasma to the surface of the substrate and impart energy to the atoms on the surface of a growing film. This bombardment by the ions provided the energy necessary to move atoms around on the surface of the substrate, which could result in well adhered dense films, which had not been possible before with PVD processes without heating the substrate to high temperatures.

Early ion plating work typically involved the use of an evaporative source (heated crucible, electron beam, and now cathodic arc evaporation, etc.) to produce the flux of the material, but it was quickly learned that ion plating was not restricted to evaporation processes. Sputtering sources and laser ablation sources could also be used to produce the coating flux, and the plasma around the substrate could be the source of ions to be attracted to the substrate to produce the ion peening effect.

Initially the ion plating process used high substrate bias voltages in the range of 1-2 kV to attract the ions, but such high voltages are not needed to get the beneficial effects of the ion plating process. Today the negative substrate bias potential is typically in the 50 to 150 V range.

Ion plating goes by many different names. It is called of course ion plating, but it is also know as ion assisted deposition, plasma enhanced deposition, plasma assisted deposition, bias sputtering, and many other names. No matter what it is called it is still the same process of using ions to impart energy to a growing film to increase the density of the deposited film and to improve its properties.

In this author’s estimation, ion plating is one of the key PVD inventions. Without ion plating, it would not be possible to produce the high quality films that we do today on a routine basis. It is safe to say that virtually all hard tribological coatings deposited today are done with ion plating.

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**Early Hard Coatings Systems**

In the late 1970s, the use of ion plating to produce hard coatings became an industrial reality. Balzers [5] came out with their low voltage electron beam ion plating system for the deposition of TiN, which set the quality standard for years for TiN coatings. Ulvac also introduced their hot hollow cathode system for the deposition of TiN based on ion plating principles.

About the same time that Balzers and Ulvac became active in PVD hard coatings, the cathodic arc evaporation process was revealed to the western world. Much of the early work on cathodic arc systems was done in the former Soviet Union, and around 1980 a new company called Multi-Arc introduced the technology in the United States.

There was a distinct advantage with the new cathodic arc technology that was not available at that time with other PVD deposition processes, which was the production of a very high degree of ionization of the evaporated material. Bias deposition was still used to produce dense films, but it was not necessary to create a secondary plasma around the substrate as it had been with other ion plating processes. The cathodic arc process produced its own plasma from which ions could be extracted.

There was one major drawback to the cathodic arc process as it was originally introduced. It produced, in addition to the ion flux a large flux of particles, the so-called macroparticles that could become imbedded in the growing film. These macroparticles degraded the quality of the deposited films, and depending on the application could prevent cathodic arc evaporation from being used. However, in many applications the cathodic arc process produced acceptable results in the deposited films. The cost of a cathodic arc deposition system is usually less expensive than the cost for other PVD deposition systems, and this low cost for the equipment combined with acceptable performance results for arc deposited coatings has made cathodic arc deposition one of the primary PVD coating techniques for depositing tribological coatings.

A great deal of work has been done to reduce or eliminate macroparticles from the cathodic arc process. Much progress has been made in this area, and today with filtered cathodic arc deposition equipment it is possible to deposit virtually macroparticle free films. However there is a cost to this filtering. It adds to the expense of the equipment, and it reduces the deposition rate.
Other PVD coating techniques were making their mark for the deposition of hard tribological coatings by the early 1980s. The triode high voltage ion plating process had been introduced in the UK [6], and TecVac had produced a commercial version of the process. By using a hot filament triode system, the ionization of the evaporated material had been decoupled from the electron beam evaporation process, and it was possible to achieve both high deposition rates and high ionization of the evaporated material with this technique.

Sputter Deposition of Hard Coatings

Sputtering in the early 1980s was an important deposition technique for the micro-electronics industry, but it had yet to make its mark in the hard coatings industry. Two factors held it back. The first factor was that the density of the hard coatings produced with magnetron sputtering was less than that produced by the competitive PVD techniques. Although ion assisted deposition did help the density of the films, they usually were not fully dense. The hardness of the coating along with its performance was not as good as what was being produced by the other PVD processes.

Even though the deposition rate for elemental materials had been increased by a factor of 10 with the introduction of magnetron sputtering in the 1970s, the deposition rate from compound targets or the deposition rate during reactive sputtering was very low due to the higher binding energy of the atoms in the compound material. Sputter deposition of hard coatings, which are compound materials, was not economically viable when compared to the other hard coating processes. Fortunately solutions emerged in the early 1980s that overcame both of the above mentioned problems for sputter deposition of hard coatings.

Unbalanced Magnetron Sputtering

The solution to the density problem for sputter deposited hard coatings came from the invention of unbalanced magnetron sputtering by Window and Savvides [7] from CSIRO in Australia. They showed that by making one of the sets of magnets in the magnetron cathode, either the inner or the outer ones, stronger than the other set that it is possible to create a strong secondary plasma away from the target surface in the area when the substrate resides. In practice, it is normally the outer set of magnets that is strengthened, and by doing this it is possible to increase the ion current density at the substrate substantially.

The real advancement with unbalanced magnetron sputtering came when multiple unbalanced magnetrons were used together in the same sputtering chamber. The pioneering work with unbalanced magnetron sputtering took place on both sides of the Atlantic Ocean with work being conducted at Northwestern University in Evanston, Illinois and at Teer Coatings in the UK. Suzanne Rohde and co-workers [8] showed that with two strongly unbalanced magnetrons in the closed field condition that it was possible to increase the ion current density at the substrate by a factor of 10 or more compared to using balanced magnetrons under similar sputtering conditions. The substrate bias current density with closed field unbalanced magnetron sputtering was equivalent to what was being achieved with competing commercial PVD hard coating techniques. Fully dense, well-adhered hard coatings with excellent properties can now be deposited with unbalanced magnetron sputtering [9].

While the work was going on at Northwestern University on unbalanced magnetron sputtering development, Dennis Teer at Teer Coatings was doing very similar work. He too realized the importance of unbalanced magnetron sputtering, and his company obtained the patent rights [10] to multi-cathode unbalanced magnetron sputtering.

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Perhaps the person who did the most to turn multi-cathode unbalanced magnetron sputtering into a commercial reality was Dr. W.-D. Münz when he was working for Hauzer Techno Coating in The Netherlands. He recognized the importance of unbalanced magnetron sputtering, but he also recognized the importance of features of cathodic arc deposition. He combined the best features of both coating techniques when he championed the development of the Arc Bond Sputtering (ABS) multi-cathode unbalanced magnetron sputtering system [11]. This coating system has become an important tool for many tribological coating applications such as hard coating of tools and for decorative and functional coatings for hardware and plumbing applications.

The other issue that held back the use of sputtering as a viable commercial deposition technique for the deposition of hard coatings was its deposition rate for these materials. There are two ways to deposit hard coatings via sputtering. The first is to use a target made of the hard material, and the other way is to reactively sputter a metal target.

Using a compound target made of the hard material has several drawbacks. The fabrication of the target can be difficult because to achieve full density in the target involves very often sintering of very high temperature materials. If the target is produced with less than full density, gas can be trapped in the target, and this gas can be released suddenly during the process, very often resulting in an arc condition on the target. Arcs lead to droplet ejection from the target, and these droplets then become imbedded in the film, reducing its quality.

The other and more important issue with sputtering from a compound target is that the sputter yield from the compound material is usually much less than the yield from an elemental metallic target. The sputter yield is inversely proportional to binding energy between atoms in the target, and the binding energy is much higher between atoms in a compound target than it is between atoms in an elemental target. For example for an equivalent target power, the deposition rate from an aluminum target is about 30 times higher than it is from an alumina target. For industrial processes, throughput is extremely important, and low deposition rate processes lose out to higher rate processes.

Reactive Sputtering

Reactive sputtering is another way to produce a compound film from a sputtering process. During reactive sputtering, an elemental target is sputtered in an inert gas atmosphere (most often argon) while a second gas, which will react with the sputtered material to form a compound, is purposely admitted to the chamber during the deposition process. For example, an aluminum target can be sputtered in an argon/oxygen atmosphere to form alumina (Al₂O₃), or titanium can be sputtered in an argon/nitrogen atmosphere to form titanium nitride (TiN).

Although it is possible to deposit many different compound films with reactive sputtering, historically when flow control of the reactive gas has been used there has been a problem with the deposition rate. When the flow of the reactive gas approaches the level where a good stoichiometric film is being deposited on the substrate, the same film will form on the surface of the target. Since the deposition rate for the compound is much less than that for the elemental target, the sputtered flux decreases, and the partial pressure of the reactive gas suddenly increases as the target transitions from sputtering from a metallic surface to sputtering from the target surface that is covered with the compound, which is the so-called poisoned state of the target. In addition to the loss of deposition rate, the composition and properties of the deposited film may be less than optimal.

With flow control of the reactive gas, there is a whole range of compositions of the deposited film that cannot be obtained. The transition from the metallic state to the poisoned state occurs very quickly, and with flow control it is not possible to operate in the transition zone between the metallic and poisoned states of the target.

Reactive Sputtering Partial Pressure Control

In the late 1970s and the early 1980s, work was being carried out to find a solution to the loss of rate problem with reactive sputtering. Three groups made particular contributions to solving this problem, and they came up with three different approaches to controlling the partial pressure of the reactive gas during the reactive deposition. Schiller and co-workers [12] at the then Manfred von Ardenne Institute in Dresden, Germany found that if they used the intensity of an optical emission line from the sputtered material as a feedback signal that they could control the partial pressure of the reactive gas with a fast responding control system, and they could work in the transition region between metallic and poisoned states of the target.

Sproul and Tomaszek [13] took a different approach to controlling the partial pressure of the reactive gas. They used a differentially pumped mass spectrometer to provide a feedback signal to the fast acting partial pressure control system, and they too found that they could work in the transition region between the metallic and poisoned states of the target during the reactive sputtering of a compound film. There were no forbidden regions for the reactive process.

Sproul [14] also found that it was possible to achieve relatively high deposition rates by controlling the partial pressure of the reactive gas. For a nitride like TiN, they were able to achieve a deposition rate for the nitride that equaled the metal deposition rate. In later years with this same type of control system when used in conjunction with pulsed DC power, Schneider et al. [15] were able to show that they could deposit alumina at 70% of the metallic rate, which was a significant increase in rate compared to the poisoned deposition rate.

The third approach to controlling the partial pressure of the reactive gas came from Affinito and Parsons [16]. They found that if they operated in a constant power mode on the power supply that the cathode voltage changed as the partial pressure of the reactive gas changed. They looked at the reactive deposition of aluminum oxide and aluminum nitride, and they observed that as the partial pressure of the reactive gas increased, the cathode voltage decreased. Using a feedback signal that was proportional to the cathode voltage, they were able to control the partial pressure of the reactive gas for the deposition of aluminum nitride. However, at that time their control system was not fast enough to respond to changes in the partial pressure of oxygen during the deposition of aluminum oxide.

Thus by the mid-1980s, there were three methods for controlling the partial pressure of the reactive gas based on optical emission, mass spectrometer, and cathode voltage feedback signals. Today all of these feedback signals are still being used for controlling reactive sputter depositions, and there is a fourth sensor, the lambda sensor, that is also used. The lambda sensor is a solid state sensor that only works for oxygen, but it does a good job with that reactive gas.

There are advantages and disadvantages to each reactive gas sensor. The most versatile sensor is the differentially pumped mass spectrometer. It can measure all gases within its mass to charge ratio range, and it can be helpful with many other aspects of the process besides providing a partial pressure feedback signal. Of the four sensors, it can do the most, but it is the most expensive sensor.

The least expensive sensor can be the cathode voltage feedback signal. It is usually available from the power supply, but one must be sure that the signal is updated in a timely manner especially for
The cost of an optical emission sensor for reactive sputtering is modest. The cost of a sensor is in the range of $1,000 to $5,000 depending on whether or not a spectrometer or a simple filter/photo diode sensor is used.

The lambda sensor relies on the conduction of oxygen ions through a solid state electrolyte to generate the partial pressure signal. The lambda sensor works only with oxygen, but it works well with most reactive oxide depositions. The cost of the lambda sensor is about the same as the cost for an optical emission sensor.

Power Supplies for Reactive Sputtering
Unbalanced magnetron sputtering and partial pressure control of the reactive gas have been very important in the use of sputtering for the deposition of hard coatings. Recent advances in power supply technology have also improved the performance of sputter deposition systems. The introduction of switching power supplies with very low stored energy has greatly reduced the damaging effects from arcing on the target. An arc is a low voltage, high current condition on the target in which the current is concentrated in a very small area. This small area is quickly heated to the point where the surface melts and droplet are ejected from the melted area. These droplets, if they become trapped in the film, degrade the quality of the film or render it useless. If an arc forms, the switching power supplies sense the arc and take steps to clear it thus minimizing the damage from an arc.

For reactive sputtering deposition of insulating films such as aluminum oxide, the use of pulsed DC power or mid-frequency AC power has made it possible to deposit these films while preventing arcing that would occur if DC power were used. It is not necessary to use RF power with all its complications and extra costs.
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Pulsed DC power can also be used instead of RF power for the substrate bias when depositing insulating films. There is a thickness limitation of about 3 to 5 μm for the use of pulsed DC power for the bias for insulating films, but for many applications this is not an issue. For thicker films, RF power should be used for the bias to prevent arcing on the substrate.

For those interested, more details about controlling reactive sputtering processes can be found in several recently published articles [17-21].

High Power Pulsed Magnetron Sputtering

There is a relatively new development in power supply technology that potentially will have a significant positive impact on the sputter deposition process and the production of hard tribological coatings. This new development is high power pulsed magnetron sputtering (HPPMS), which is also known as high power impulse magnetron sputtering (HIPIMS). It was first introduced by Dr. Vladimir Kouznetsov [22], and the pioneering research and development work on this technology was done at Linköping University in Professor Helmersson’s group [23-26]. Other pioneering work on HPPMS was started at Sheffield Hallam University by Professor W.-D. Münz, and after his retirement is now being carried on at Sheffield Hallam by Professor Hovsepian and Dr. Ehiasarian [27-30]. In the U.S., some of the early work on HPPMS was conducted by Christie and co-workers at Advanced Energy Industries, Inc. [31-33].

With HPPMS, a large energy pulse is applied to the sputtering cathode for a short period of time, and as a result of this energy pulse there is a high degree of ionization of the sputtered material. The degree of ionization depends on the material being sputtered and the peak power density. To obtain good ionization, power densities of 1-3 kW/cm² are applied to the target for a peak width time on the order of about 150 μsec.

Depending on the size of the target, the peak power can and does reach the megawatt range. Even though the peak power can be quite high, the average power delivered to the target is similar to conventional magnetron sputtering processes. The average power is a function of the peak power and the repetition rate of the pulse. Typical duty cycles are less than 1%. The pulse of HPPMS is that it can provide ionization levels that approach those in cathodic arc deposition, but it can do it without producing the macroparticles. Ionization values up to 90% have been reported for titanium [23].

The one disadvantage of the HPPMS process following the pulse method of Kouznetsov is that there is a significant loss in deposition rate compared to DC sputtering for an equivalent average power. Sproul et al. showed that the HPPMS deposition rate is only about 25 to 30% of the DC rate for an equivalent power level [32].

Recently it was reported that there is a way to overcome the rate problem with HPPMS. By modulating the power within a pulse, Chistyakov et al. [34,35] showed that they could achieve deposition rates for their pulsed modulation power (MPP) version of HPPMS that equal or exceed the DC rate. The MPP process applies a pulse within a pulse to drive the plasma into a strongly ionized state from the starting weakly ionized state, and there is a high degree of ionization of the sputtered material produced in the strongly ionized plasma state. Typical pulse lengths for the MPP process are on the order of 1-3 msec, and the peak power density values are typically in the 100-1000 W/cm² range.

The challenge for materials researchers around the world is now to learn how to use the HPPMS processes to their advantage. It is well understood that the energy of the depositing species determines the structure and properties of the deposited film. In the HPPMS process, a highly ionized flux produced in the HPPMS processes arrives at the substrate surface without the degrading macroparticles of the unfiltered cathodic arc processes. In this author’s opinion there are tremendous opportunities to use the energy of these ionized fluxes to produce films and structures that have not been possible before. HPPMS has opened up a whole new world of opportunities for the PVD deposition of hard tribological films.

Today reactive cathodic arc deposition and reactive multi-cathode unbalanced magnetron sputtering are the two PVD main methods used to produce deposit hard coatings. In addition, plasma enhanced CVD processes, which are done in vacuum deposition systems, are used frequently to produce many of the diamond-like carbon films. It has been the development of these coating systems that has made it possible for there to be a hard tribological coatings industry today.

A look at the hard tribological coatings produced over the past 30 years in PVD systems will be given in a companion paper to this one. It will be available in the 50th Annual Technical Conference Proceedings of the Society of Vacuum Coaters.

References


William Sproul is the founder of Reactive Sputtering, Inc. Prior to that he was with Advanced Energy Industries, Inc. He is the inventor of the high rate reactive sputtering process, and he has been instrumental in the development of reactive deposition of both insulating and conductive films. He received his Sc.B., Sc.M., and Ph.D. degrees in Materials Science Engineering from Brown University.

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