Cathodic Arc Plasma Deposition

André Anders

Lawrence Berkeley National Laboratory, University of California,

1 Cyclotron Road, Mailstop 53, Berkeley, California 94720

aanders@lbl.gov

Abstract

Cathodic arc plasma deposition is one of oldest coatings technologies. Over the last two decades it has become the technology of choice for hard, wear resistant coatings on cutting and forming tools, corrosion resistant and decorative coatings on door knobs, shower heads, jewelry, and many other substrates. The history, basic physics of cathodic arc operation, the infamous macroparticle problem and common filter solutions are reviewed. Cathodic arc plasmas stand out due to their high degree of ionization, with important consequences for film nucleation, growth, and efficient utilization of substrate bias. The overview concludes with a compilation of typical applications and coating materials.

Introduction

Cathodic arc plasma deposition is one of the oldest and one of the most modern, emerging technologies. This is an apparently contradictory statement. I will span a view from reaching more than a century ago to recent research in the hope to transpire some excitement and background knowledge.

Although cathodic arc plasma deposition belongs to the family of physical *vapor* deposition (PVD) techniques, I deliberately called it *plasma* deposition to emphasize an important feature: energetic condensation from plasma ions, as opposed to condensation of atoms from the vapor phase. The synthesis of films from ions, each carrying substantial kinetic and potential energy, can lead to film properties that are unique.

As the name suggests, cathodic arcs are determined by cathode processes. Indeed, cathode processes are quite different than one is used to from other, more "moderate" forms of discharges. Current densities, and associated power densities at cathode spots are extremely high, and this is true despite the characteristic low cathode fall voltage of typically 20 Volts. The electron emission processes involve violent, non-stationary phases, leading to the destruction of the electron emission center. The phase transition from the solid cathode material to plasma is precisely what enables operation of the arc discharge and what makes cathodic arcs plasma deposition possible.

In the literature, the reader may have come across the terms "vacuum arcs" and "cathodic arcs" and wonder what the differences are, if any. As Lafferty pointed out [1], the term "vacuum arc" is an oxymoron: if there is an arc there is no vacuum, and where vacuum is there is no arc. The term "vacuum arc" implies that there was vacuum between electrodes before and after the arc discharge. The instantaneous plasma

pressure in cathode spots exceeds atmospheric pressure by orders of magnitude. It is therefore not surprising that cathode processes observed from vacuum arcs do also apply for arc discharges in the presence of gas between electrodes. The gas, though, may have secondary effects, especially on the surface conditions of the cathode. Traditionally, "vacuum arc" is used to emphasize the absence of any significant gas pressure before the discharge, and "cathodic arc" is generic for a vacuum arc or an arc in background gas.

This explanation, however, is complicated by the possibility that the cathode can operate in other modes, e.g. in the thermionic mode. Additionally, the anode is not always a passive electron collector but may emit anode vapor and plasma, which is called "anodic arcs" [2] in the coatings world, and "intense arcs" in the switching world [3]. In this article we focus on cathodic arcs with globally cold cathodes, where plasma is produced at non-stationary cathode spots.

Cathodic arc plasma deposition is a coating technology with great potential because cathodic arc plasmas are fully ionized with very energetic ions, promoting adhesion and the formation of dense films. Though, there are disadvantages and problems too. Films may be under high compressive stress, and so-called "macroparticles" may be incorporated. The macroparticle problem has prevented that cathodic arc plasma deposition is used in high-tech applications – but that may change with the perfection of macroparticle filters.

Macroparticle filters do not only remove macroparticles, as their name suggest, but also neutral atoms that may be present from evaporating macroparticles and the still hot craters on the cathode, the previously active sites of cathode spots. The streaming, expanding filtered plasma contains only ions and electrons. Bias applied to substrates can therefore very effectively be used to affect the energy of the condensing plasma. These and many other details and features will be discussed in the remainder of this article.

A brief history of cathodic arcs

The history of cathodic arc plasma deposition may be traced back to the year 1800 when Alessandro Volta announced his invention of a "pile" which, for the first time, allowed researches to produce and use continuous electric current. In the Voltaic pile, pairs of disks of dissimilar metals are immersed in a weak-acid electrolyte. Volta's battery enabled an unprecedented increase in interest and research in electricity, reaching culmination points in Michael Faraday's discovery of electromagnetic induction (1831) and James Maxwell's theory of electromagnetism (1873).

An arc can be obtained when a Voltaic battery is short-circuited: by pulling apart two horizontally aligned graphite electrodes in air, Sir Humphry Davy observed in 1810 the characteristic bright discharge forming an arch (due to convection), hence the name arc. Davy is commonly credited with the invention of the arc

though, independently and years earlier, the Russian Vasilii V. Petrov (1761-1834) reported in 1803 about this form of discharge [4]. A separate paper honoring the 200th anniversary of arc discharges is in preparation.

Faraday investigated in 1838 the ability of a given gas in a glass tube to pass the discharge current in terms of the pressure of the gas. These studies *in vacuo* led to the discovery what is today known as the Faraday dark space, a characteristic zone of a low pressure glow discharge. Unfortunately, current and voltage were not well determined at this time so we are now forced to make our best guess, based on information of the electrical circuits used, whether an arc or glow discharge was observed. This is difficult, for instance, in the experiment of Julius Plücker who observed in 1858 that when the cathode was made from platinum, "small particles of platinum were torn off…and deposited upon the internal surface of the glass bulb enclosing the electrode…this glass bulb becomes gradually blacked, and after the long-continued action, the bulb…becomes coated internally with a beautiful metallic mirror" [5]. Did Plücker observe what we call now macroparticles? Or was he referring to indiscernible particles (atoms) that were sputtered?

Sputtering in glow discharges was observed first by William Robert Grove in 1852. In contrast to arc discharges, the voltage between glow discharge electrodes is relatively high (in typical systems greater than 100 V), while the current low (less than 1A). It was most likely pulsed sputtering that Arthur Wright [6] used in his 1876 experiments when he produced a large number of thin films, perhaps the first systematic study of metal coatings by discharges and plasmas (see also discussion by Boxman [7]).

Let us make a big step and enter the area of modern cathodic arc coatings which began with a series of patents by Thomas Alva Edison. Edison was working on perfecting his phonogram. He was looking for practical ways of making copies from original phonogram recordings. It appears that he was the first who explored cathodic arc coating as described in his patent application "Art of plating one material with another," filed on January 28, 1884 [8] (Figure 1). The application was initially declined due to apparent prior art by Wright. Edison filed another application in 1888, "Process of duplicating phonograms," where he narrowed his claims [9]. The latter patent was granted first, on October 18, 1892, and so it constitutes the first granted patent that describes cathodic arc coating. The earlier application was finally granted in 1894, after Edison limited its claims to a continuous discharge in order to distinguish his claims from Wright's pulsed work (which most likely was sputtering). Ironically, a continuous arc has the "danger of injuring the vary delicate phonographic-record surface, particularly from the heat of the arc," as he admitted in his 1902 patent "Process of Coating Phonograph-Records," [10] and therefore Edison decided to use sputtering for the production of phonogram copies.

Cathodic arcs remained a subject of research with tough challenges, with application in switching (mercury switch) rather than coating. Researchers, such as Tanberg [11], developed clever techniques to uncover the

secrets of cathode spot physics. As part of the Manhattan Project, vacuum arcs were investigated in the 1940s for uranium isotope separation although ultimately it was not used.. Practically nothing has been published about this then-classified research.

With the growth of post WWII industrial demands, cathodic arc coating technology was rediscovered. Arc plasma sources for DC operation were developed. Of particular importance are the patents by Snaper [12] and Sablev and coworkers [13] because they describe the basic design of these sources for the years to come and used by leading companies like MultiArc. While DC sources became the "work horses" for coatings applications, pulsed sources were also developed and studies, for example by Gilmour and Lockwood [14].

The 1960 and 1970s were characterized by a number of important improvements of experimental techniques applied to cathodic vacuum arc research. Milestone papers describing cathodic arc plasmas as energetic with multiple charge states were published by Kesaev [15], Plyutto and co-wokers [16], Davis and Miller [17], and Lunev and coworkers [18]. Daalder systematically investigated size and emission angle distribution of macroparticles [19]. Jüttner and coworkers [20] showed the effect of the cathode surface conditions on the appearance and type of cathode spots. First books appeared dedicated to the science and technology of cathodic arc discharges [1, 21, 22].

In the Soviet Union of the 1970s and 1980s, arc technology was declared a "key technology" and, as a consequence of this political decision, thousands of arc evaporators were build and a large number of researchers and engineers were educated in arc technology, with consequences seen until today. Many of today's patented and commercial coating apparatus have their origin in previous Soviet technology.

A research group in Kharkov, Ukraine, which was part of the Soviet Union at that time, developed the first filtered arc system [23]. It consisted of a large 90° duct with a magnetic coil around it. This classic design and its derivatives have been used by several research group and companies (see the section on filters below). With the invention of macroparticle filters, films of greatly improved quality could be deposited.

In the early 1980s, Adler and Picraux experimented at Mission Research Corporation with pulsed cathodic arcs and substrates at very high negative bias, essentially performing the first metal ion implantation based on the plasma immersion concept [24]. This concept was later modified into a hybrid implantation and deposition technique [25].

In their book on pulsed vacuum discharges, Mesyats and Proskurovski [26] summarized research on explosive electron emission, which is crucial for the understanding of not only pulsed but DC-arcs on cold cathodes. Later, Mesyates [27] went on formulating his Ecton model according to which micro-explosions

on cathode surfaces occur in small but characteristic actions or power portions. The concept of sequential explosions is supported by high-resolution spot diagnostics using advanced laser techniques [28] and high-speed cameras [29].

Returning to the applied approach to cathodic arcs, one needs to include the use of cathodic arc plasmas for ion etching through sputtering. Münz and coworkers [30] introduced Arc Bond Sputtering (ABS) as a combination of ion etching with cathodic arc plasmas and deposition by magnetron sputtering. Siemroth, Scheibe, and others [31, 32] developed a laser-triggered arc system (Laser Arc) for the deposition of metal and diamond-like carbon multilayers. In 1995, Boxman, Sanders, and Martin [33] published their Handbook on Vacuum Arc Science and Technology, which has become a standard in the field. Recently, modern developments target the perfection of macroparticle filters, large area coatings, the development of better coating material systems, especially multilayer and alloy systems, and the penetration of high-tech fields such as magnetic media, microelectromechanical system (MEMS), and metallization of semiconductors.

The physics of cathode processes

Cathode processes are at the heart of cathodic arc plasma deposition. Cathodic arc processes have features that are surprising or strange even for scientists and engineers familiar with discharges and plasmas in general. The plasma "root" or "attachment" on the cathode is localized in tiny spots that move randomly or steered on the surface, depending on the absence or presence of an external magnetic field. A central quantity, and subject of intense discussion and research, is the current density of cathode spots. It is important because the current density distribution determines the power density distribution, which, in turn, governs all processes of electron emission, phase transitions, and plasma production.

Although the discussion is not yet completed, there is evidence for a cathode spot structure containing interacting activity centers called fragments (see [29] and references therein). The current density of cathode spot is of order 10^8 A/cm^2, with possibly even high peaks at fragments, and somewhat lower values if averaged in time and over the spot-surrounding area. Since the area of a spot is difficult to define, the current density as a single value may be ill defined; and it may be better to use the concept of a space and time-dependent current density distribution. Even when using the simplified current density approach, we realize that the associated areal power density is of order 10^9 W/cm^2 because the cathode fall is of order 20 Volts. This power density is sufficient to transform cathode material from the solid to the plasma phase in an extremely short time period of 10-100 ns [29]. It is appropriate to call a phase transition of that short duration an explosion. The nanosecond time range constitutes the shortest characteristic time of cathodic arcs. Fluctuations on longer time scales also appear due to the statistical superposition of numerous elementary events. The fractal model appears to be a good approach to a more comprehensive understanding – still to be worked out.

Figure 2 shows an absorption photograph of cathode spot. In this example, the cathode is a needle whose tip is positioned very close to the anode. The small dimensions were chosen to make it possible to "catch" the spot where the camera is looking with high-resolution. The exposure time for this photo was 0.4 ns (not a printing mistake, indeed 4×10^{-10} s), achieved with back-illumination by a pulsed dye laser [28]. From pictures like this we have learned that spot formation occurs in nanoseconds and current densities are as high as described above.

The explosive phase transformation is characteristic for cathodic arcs and unusual for other discharge types. The electron emission mechanism is therefore also unusual. None of the traditional mechanisms (thermionic emission, field emission, Schottky-enhanced thermionic emission) is responsible but what has been called "explosive electron emission" [26, 34]. Electrons are emitted by the synergetic presence of high temperature, high electric field, and via ionization of cathode material. It is precisely the concentration of electrical power that makes operation of this arc mode possible. Cathode spots have to fulfill the function of electron emission centers *and* provide the condition for self-sustained arc operation through plasma generation. The presence of dense metal plasma "squeezes" the cathode fall voltage into an extremely thin layer, thereby localizing power dissipation.

So why is the cathode spot structure non-stationary? A micro-explosion is changing the surface topography and is rapidly heating the zone beneath the spot. Besides changes of the local conductivity, the spot area will increase with time due to heat conduction. An increasing area implies a decreasing current density, which in turn will reduce the power density. The amount of cathode material transferred by the explosive phase transition will become less in time, which causes the local plasma density to drop. Therefore the cathode fall will be less "squeezed" to the surface, and thus the electric field strength and power density will decrease with time, reducing the current density of electron emission from the solid. The peak temperature will also fall, further reducing electron emission. The spot activity will go from its nanosecond "explosive" phase to a slower "evaporative" phase.

Eventually, the electron emission and plasma density in the discharge gap would be reduced to a point where the discharge is threatened to cease. The voltage between anode and cathode (burning voltage") increases, due to reduced conductivity, counteracting the loss of electric field strength at the surface. Now, either the discharge ceases indeed, or the increased voltage combined with the still-dense plasma near the cathode enables a favorable location at the surface, such as a microprotrusion, to emit electrons. Such favorable location is heated by both Joule heat of the electrons in the metal and by the energy of ion bombardment. Increasing temperature leads to a runaway situation: More electrons are emitted, leading to enhanced ionization of the location's vicinity, leading to even greater ion bombardment, temperature

enhancement and electron emission. The thermal runaway will lead to explosive destruction of the microprotrusion on a nanosecond timescale, and thus a new spot is born in its explosive phase.

Although there are a number of differences between pulsed and continuous cathodic arcs, it is important to note that these non-stationary, cyclic cathode processes occur regardless of the arc discharge duration. What appears as macroscopic "motion" of the cathode arc spot is more accurately described as a rapid sequence of ignition and extinction of active spot locations (Figure 3).

Due to the extremely high power density, the metal plasma produced in the explosive phase is fully ionized, in fact, it often contains not only singly but multiply charged ions. Charge state distributions of cathode arc plasmas in vacuum have been extensively studied (e.g. [35, 36]) and they can be explained by a Saha model, or more precisely the model of Partial Local Saha Equilibrium (PLSE) [37]. One argument for full ionization is the necessity of a bell-shaped ion charge distribution. For instance, if the plasma contains more doubly charged ions than singly charged ions, it is unphysical to have more neutrals than singly charged ions *if* they come from the same source. The last restrictive qualification leaves the door open for significant amounts of neutral vapor to exist, even if the statement was made that the cathode spot plasma is fully ionized♦. There are two sources of neutral vapor: evaporating macroparticles [38, 39] (macroparticles will be discussed below) and still hot, previously active spot locations. Strictly speaking, the cathodic arc plasma contains a superposition of fully ionized plasma from active spots and neutral vapor from macroparticles and cooling spot craters. The amount of neutral vapor will greatly depend, among other parameters, on the vapor pressure of the cathode material. Not much has been published about the ratio of ionized plasma and neutral vapor.

The cathode spot plasma is characterized by very high density and temperature and therefore pressure, which indeed can exceed atmospheric pressure by orders of magnitude. Driven by the very high pressure gradient near the spot, in conjunction with electron-ion coupling, ions are accelerated to supersonic velocities in the order of 10^4 m/s. A more detailed investigation showed that the ion velocities for vacuum arcs can be correlated with the arc voltage [40], which in turn is correlated to solid state properties of the cathode, especially the cohesive energy ("cohesive energy rule" [41]). Ion energy plays an important role for the quality of the coatings, as discussed in the section on energetic condensation.

There exists a minimum current that is needed for a stable, self-sustained arc operation. Discharge currents lower than what is called the "chopping current" will lead to spontaneous extinction of the arc. A minimum current is required to ensure sufficient plasma production providing a very high likelihood of ignition of a new cathode emission center when the power density at the active center has dropped. This

♦There are exceptions: no conclusion can be drawn for plasmas dominated by singly charged ions, such as carbon or lithium.

minimum current depends on the cathode material as well as on the surface state of the cathode. For example, the chopping current for pure titanium is about 50 A [42].

The parameters of cathode processes depend indeed greatly on the surface state, especially on the presence of non-metallic layers such as of oxides, nitrides, hydrides, carbides, and hydrocarbons, which depends on vacuum quality, treatment history, and temperature [43]. If an arc is burned on a non-conditioned, "fresh" cathode surface, the current per emission center, or arc spot, is much smaller than the current per spot in the case of a chemically clean metal surface. The crater erosion pattern is strikingly different, see Figure 4. In the present of a non-metallic layer, craters produced by arc spots are smaller and separated from each other. In contrast, craters on clean metal surfaces are larger and form continuous chains. Traditionally, the spots are called of type 1and 2, respectively. One can easily remember this order: an arc starts burning with type 1 spots, the action of ion bombardment and heat cleans the surface and the spot transitions to type 2 (Figure 4).

The amount of plasma produced was found to be directly proportional to the arc discharge current [44]. Interestingly, other parameters such as burning voltage, ion velocity, and mean ion charge state do *not* noticeably depend on the arc current[♠]. This may be surprising at first sight but it becomes plausible if one considers that higher currents lead to "spot splitting" or a larger *number* of simultaneously active cathode spots, where each of the spots maintains approximately the same operational mechanism.

Based on this experimental fact and sophisticated time dependent models, Mesyats introduced the concept of a minimum action that is needed to achieve electron emission via the explosive mechanism, and he termed the elementary explosive event "ecton" [34]. The ecton model, though, is not widely used, perhaps because no new practical guidelines have been derived from it.

The plasma on its journey to the substrate

As pointed out, ion acceleration is mainly due to the electron and ion gradients which are strongest right at the cathode spot. Therefore, the vacuum arc plasma drift velocity is approximately constant when the plasma travels to the substrate. If a cathodic arc is operated in a gas, such as nitrogen, ions may suffer collisions with gas molecules and therefore slow down. Ionization of background gas and reduction of ion energy depend on the pressure and type of gas. As a rule of thumb, if the background pressure approaches or even exceed 1 mTorr (0.1 Pa), the mean free path becomes smaller than the size of the coating system and thus a strong influence of the gas can be expected.

[♠] This is not true for high currents, e.g. arc with currents in the kiloampere region, when anode activity occurs and when the magnetic self-field cannot be neglected.

The plasma expands into the vacuum or low gas pressure region ambient. For free expansion, i.e. expansion not dominated by external magnetic fields and interaction with gas, the plasma density falls as d^2, where d is the distance from the cathode spot [44]. The more the plasma expands, the lower its density and associated deposition rate, but the larger the area that can be relatively uniformly coated.

The collision rates in an expanding vacuum arc plasma drop rapidly. Indeed, the rate for inelastic collisions becomes very small at even small distances from the cathode spot, and therefore the ratios of ion charge states is practically constant in the expanding plasma. The plasma is in ionization non-equilibrium and exhibits a "frozen" (i.e. constant) charge state distribution [45]. In the presence of background gas, or strong external magnetic fields, the model of a frozen charge state distribution does not apply. The background gas can be ionized through electron impact ionization and charge exchange collisions. The ionization of background gas is greatly enhanced if a magnetic field is present because the path length of electrons is multiplied through gyro-motion. Magnetic fields are used, for instance, to collimate and guide the plasma toward the substrate, or to facilitate macroparticle filtering.

Macroparticles

Macroparticles are liquid or solid debris particles that are produced at cathode spots along with the plasma. In his cathode spot model, Jüttner [46] explained particle formation through the action of plasma pressure on the melted cathode material that is present between the dense plasma and the relatively cold cathode body (Figure 5). The production of macroparticles particles is therefore inherently connected to the existence of non-stationary cathode spots.

Macroparticles are named this way to emphasize their very massive nature compared to electrons and ions. Numerous studies have been performed to determine size and velocity distributions as a function of cathode material and temperature, arc duration and current amplitude, and the presence of external magnetic fields, e.g. [17, 19, 47, 48]. Summarizing the main finding of these studies one can state that the size distributions are very wide, from a few nanometers to about the maximum size of craters, i.e. micrometers. Smaller macroparticles are much more frequent than larger once. Materials of low melting point have much more and larger macroparticles. Macroparticles move essentially along straight trajectories. The negative charge acquired while moving through plasma plays a role only for the smallest macroparticles.

For many years it is known that magnetically driven cathode spots produce fewer particles, which can be attributed to shorter interaction time of the dense plasma with the cathode material at the spot location. This feature and a better control of the cathode erosion pattern lead to the development of magnetically "steered arcs" [49, 50]. Another observation is that heated cathodes [43] and cathodes of low-melting point material have a high particle erosion rate. This is plausible because the volume of the melted zone between the dense spot plasma and the cathode bulk is relatively large. Most particles are ejected at a shallow angle

to the cathode surface, while plasma emission is peaked normal to the surface. A good geometry for a plasma source is one that makes use of this "natural" particle-plasma separation.

Macroparticle Filters

Particle filters are used to separate and remove particles from the cathodic arc plasma. One important parameter of a filter is its plasma transport efficiency, which can be defined as the ratio of the number of ions leaving the filter to the number entering it. However, it is often difficult to determine the ion flux into the filter, and a less ambiguous value is the filtered ion current normalized by the arc current. It is advisable to use this "system coefficient", $\kappa = I_{i,filtered} / I_{arc}$, characterizing not only the filter but the coupled arc source and filter system. While the filter's plasma transport efficiency may (hypothetically) reach 100%, the system coefficient is typically a few percent. It is important to understand that the system coefficient can never reach 100% because electrons carry most of the arc current. For coating applications not only the absolute number of residual macroparticles in the coating is important but the density of macroparticles in relation to the film thickness deposited. In other words: the ratio of plasma and particles is decisive rather than the macroparticle particle number or density.

Macroparticle filtering is typically done with curved magnetic filters. Plasma guiding in such filters is accomplished by a combined magnetic field (electrons) and electric field (ions) mechanism. Electrons spiral along magnetic field lines, i.e., their gyration radius is much smaller than the filter size and their collision frequency is smaller than the gyration frequency: they are said to be magnetized. In contrast, ions are not magnetized because their gyration radius is greater than the inner filter radius. Although not magnetized, ions follow the guided electrons electrostatically so as to keep the plasma quasineutral. The electric potential at the filter axis is lower than the potential near the filter wall, i.e. ions are kept in a potential well, though the most energetic will escape and be lost for deposition.

Straight filters have the smallest plasma losses; they improve the plasma to macroparticle particle ratio but they do not eliminate particles because there is a line-of-sight between cathode and substrate. Eliminating the line of sight between cathode and substrate is a necessary condition for macroparticle removal.

Aksenov and coworkers [23] introduced a 90°-duct filter in the late 1970s. The duct filter consists of a curved duct surrounded by magnetic field coils generating a curved axial field; the 90° duct can also be considered as a quarter magnetic torus (Figure 6). To reduce particle transport by multiple reflections, baffels are inserted in the duct. This type of filter has been widely used in cathodic arc R&D over the last decades [51-56].

Storer *et al.* [57] found that the plasma transport efficiency decreases exponentially with the length of the filter, and that a curved filter has a shorter plasma attenuation length than a straight filter of comparable

construction and size. For good plasma transport, the duct must be biased with respect to the plasma, typically to about +10 to +25 V, an effect already noted in the pioneering work of Aksenov and coworkers [23]. This feature was recognized also by Bilek and coworkers [58], who showed that applying a positive bias to a strip electrode located near the outer wall of the interior of the duct produces a similar effect. With optimized bias (about +20 V) and at relatively strong magnetic fields (~ 100 mT), system coefficients of 90°-duct filters as high as 2.5% have been found [59].

Because plasma losses become greater for larger bent angle of the filter, it is reasonable to design a non-line-of-sight filter which has a relatively small bending angle and is otherwise straight. Such design was developed by Sanders and Falabella and commercialized by Commonwealth Scientific Corporation [60] (Figure 7) but production was discontinued in 1998.

In an effort to further reduce the flux of macroparticles, filters have been developed whose bending angle exceeds 90°. For example, one could continue to bend the filter to 180° or any other large angle [61]. The curvature of the filter may change; examples of such filters are the S-Filter [62] and the out-of-plane double-bent filter [63-65] and the compact, open Twist Filter [66]. Figure 8 shows an open S-Filter illustrating clearly plasma transport along the curved magnetic field and the separation of macroparticles due to their inertia.

For a number of commercial applications, large area coating is mandatory. Arc sources with conventional round cathodes of 3-10 cm diameter and filters with matching round cross sections are not suited for this task. One could arrange a number of such sources but the cost would be high. Alternatively, arc sources with large (≥ 1 m) cathodes have been developed on which the arc spot is driven or steered from one end to the other. Such sources can be matched with large filters of rectangular cross section. Early versions of a 90° rectangular duct filter were developed in the 1980s in the Soviet Union as part of the Cold War weapons and technology effort (Secret Soviet Author Certificate, unpublished [67]). In the United States, Welty [68] developed 90°-duct filter with rectangular cross section (Figure 9). Very large-area coatings are possible when the substrate is moved perpendicular to the long extension of the filter.

There are numerous other filter designs that use the principles of avoiding line-of-sight between cathode and substrates as well as plasma and macroparticle separation due to macroparticle inertia, e.g. the Venetian Blind Filter [69] originally developed by Ryabchikov [70]. More information on filters can be found in recent reviews [71, 72].

Continuous versus Pulsed and Switched Arcs

From a commercial point of view, the overwhelming majority of cathodic arc system operates in continuous direct current (DC) mode. The reason is the high deposition rate that can be obtained this way.

This is true for non-filtered and filtered systems. The typical arc current is between 40 A and 100 A, with the lower limit determined by arc chopping (i.e. spontaneous extinguishing of the arc discharge), and the upper limit determined by power considerations as well as enhanced macroparticle production. In principle, the arc current can be much higher, leading to proportionally higher plasma production and deposition rate but with constrains due to the power supply as well as cooling of plasma source and substrate.

For some applications, deposition with pulsed arcs can have advantages over DC operation. The power consumption can be easily regulated via the arc duty cycle (on/off ratio) rather than the arc current. Spot steering is not an issue since the arc spots travel only a limited distance from the point of ignition. Ignition can be designed to occur in the center of disk cathode with the arc spot "repelling" each other; the pulse is conveniently chosen to end when the spots arrive at the cathode rim. Pulsed arcs can be operated with very high currents, sometimes matching the average plasma production of DC arcs. For example, the plasma transport of pulsed high-current arcs (2 kA) was investigated using a duct filter similar to Aksenov's classical 90° filter. The ion current at the filter exit was very high: up to 7% of the arc current [73]. The High-Current Arc (HCA) system developed at the Fraunhofer Institute [74] operates with very high currents (peak 5 kA) and arc repetition frequencies (up to 300 Hz). For limited times, the average plasma production can even exceed typical DC values. In the HCA system, the arc is pulsed but the magnetic field coils for the 30°-filter segments are DC-operated.

Due to their relative simplicity in terms of power and cooling demands, pulsed arcs are frequently used in R&D systems. Results obtained (charge states, ion velocity, etc.) can generally be scaled or transferred to DC arcs because the cathode processes are non-stationary regardless of pulsed or DC operation. However, there are differences between pulsed and DC arcs and one has to be careful with generalizations. A prominent example of an effect important to pulsed arcs but not to DC arcs is the incorporation of hydrogen from water vapor in a coating. While coatings with very little hydrogen can routinely be obtained with DC arcs, hydrogen content of films can be surprisingly high when deposited in pulsed mode, especially when using short pulses at low duty cycle [75, 76].

Some systems operate in a switched mode which is close to DC operation using currents of 100 A or less. The arc discharge is not quite continuous because arc switching occurs to give arc spot a specific direction along elongated cathodes. Examples of such switched arcs are systems developed by Vapor Tech and by Vergason Technology, Inc. In Vergason's design [77], the cathode is a long rod where the negative contact is on one end and the trigger device on the other, which causes the arc spot to travel along the rod. By adding a magnetic field [78], the arc spot appears to travel in a spiral along the rod, see also Figure 10.

Energetic Condensation and Subplantation

Energetic condensation of ions from cathodic arc plasmas is known to lead to dense, well adherent films [55, 79]. The films can be under high compressive stress which may limit thickness possible before delamination. Stress, hardness, elastic modulus, and other properties need to be carefully considered as function of materials system and deposition parameters, especially ion energy and surface temperature.

Energetic condensation is a film growth process from species of hyperthermal energies, giving rise to desorption of loosely bonded adatoms and enhanced surface mobility. As mentioned before, cathodic arc plasma ions have an directed velocity corresponding to a kinetic energy of 19-150 eV, depending on cathode material [40]. This energy is high enough that ions arriving at the substrate surface will penetrate the substrate and come to rest *under* the surface, a process known as *subplantation* [80]. The kinetic energy of arriving particles is greater than the minimum displacement energy of the material [81] and film growth occurs by deposition of particles under the surface rather than on the surface. Additional to the kinetic energy that ions have gained at the cathode spot, ions can be accelerated in a thin space charge sheath when the substrate is biased (see below). Keeping in mind that an ion can have a charge state Q larger than 1, the average ion kinetic energy can be estimated by

$$E_{kin}(Q) = E_{kin,0} + Q\, e\, V_{sheath}\,. \qquad (1)$$

Ions bring not only kinetic energy to the substrate but also potential energy [82]. While the kinetic energy (or momentum) is important for the range of sub-surface penetration, the sum of kinetic and potential energy is responsible for substrate heating by ion bombardment. The by far largest contribution to the potential energy is the ionization energy, and therefore the total ion energy at arrival at the substrate surface is

$$E(Q) \approx E_{kin}(Q) + \Sigma\, E_Q \qquad (2)$$

The summation symbol Σ indicates that one needs to add the individual energy of the ionization steps in case of multiply charged ions [82].

When the ion arrives at the surface, they will be stopped at a loss rate of order 100 eV/nm. Good estimates of range can be obtained by computer codes using the binary collision approximation. The TRIM or SRIM code, for example, can be downloaded from http://www.SRIM.org/. The *kinetic* energy can be associated with short collision cascades and displacements. Each displaced atom will come to rest with large amplitude vibrations around its new site, a process far from thermodynamic equilibrium. Atoms involved in cascades represent an atomic-scale volume of "hot" material whose thermal energy is rapidly quenched by thermal conduction. The release of *potential* energy and its effects on film properties is less studied. Kinetic and potential energy are usually greater than the binding energy, surface binding energy, and activation energy for surface diffusion, and therefore both kinetic and potential energy can be expected to have a significant effect on film evolution and resulting film properties. In *filtered* cathodic arc deposition, the condensing species are exclusively ions, therefore, each of the atoms in the growing film

was several times subject to atomic scale heating, namely, once when it arrived, and furthermore when neighboring atoms arrived.

Subplantation growth of films leads to unique film properties, especially where different hybridization of bonds are possible. Most famous is the deposition of diamond-like carbon from filtered cathodic arcs where carbon ions from a graphite cathode can synthesize amorphous, superhard carbon films that contain mostly sp^3 (i.e. diamond) bonds. More about these films in the Applications section.

Deposition can be done in a wide range of substrate temperature. Most interestingly, cathodic arc deposition can be done at low (i.e. room) temperature, and therefore coatings on plastic are not only possible but routinely done on a large commercial scale.

Reactive Deposition

The by far most frequent application of cathodic arc plasma deposition is the reactive deposition of compound films such as TiN or TiAlN. "Reactive" refers to the establishment of chemical bonds between the metal, originating from cathode spot plasma, and atoms of a reactive gas, which is usually introduced between cathode and substrate. In most commercial systems, the gas inlet is located near the cathode with the idea that the arc plasma helps "activating" gas molecules (often nitrogen or oxygen): dissociation and electronic excitation makes nitrogen or oxygen reactive. The synthesis of a compound, though, occurs essentially at the substrate surface, as opposed in the steaming plasma, because each collision event, including inelastic, must satisfy the laws of energy and momentum conservation. This is unlikely for two-particle collisions but always possible for three-particle collisions. Therefore, reaction between metal and gas can occur at high gas pressures when three-particle collisions are frequent. At lower pressure, the surface of the substrate has the function of the "third particle," and energy and momentum conservation is not an issue.

Activation of reactive gases in the plasma or at impact on the substrate surface is usually not a problem, although current research explores the incorporation of additional gas *plasma* to make the synthesis of compound films faster and to ensure a better-controlled stoichiometric composition.

When the compound layer is formed, the metal reacts with all available reactive gases, and preferentially with those where the energy of formation is large, i.e. with the thermodynamically preferred gas species. The plasma may contain contamination such as water vapor, which is typical for high vacuum systems. This issue is especially important for pulsed plasma systems where the water layer on arc cathode and chamber wall are periodically "scrubbed" by the plasma pulse and where water vapor is partially ionized. Hydrogen can be incorporated in a film that is supposed to be an oxide or nitride, for example [76]. The

incorporation of hydrogen can greatly affect the desired coatings properties such as hardness and elastic modulus [83].

Reactive deposition is commercially done at elevated temperature. One reason is that the deposition process itself heats the substrate. Heating is often utilized to obtain the desired coating texture, for example, TiN on cutting tools is deposited at 270°C but this temperature can be reduced to 190°C. A possible side effect of elevated temperature is the reduction of hydrogen incorporation.

Biased Deposition: Plasma Ion Immersion Processing, Ion Etching, Subplantation and Ion Plating
Only charged particles are affected by substrate biasing. One of the most important advantages of cathodic arc plasmas is their high degree of ionization. Therefore, biasing is exceptionally effective and powerful in cathodic arc plasma deposition compared with other deposition techniques.

Biasing is usually performed with negative polarity as to accelerate ions and repel electrons. However, biasing can be done in various ways besides the unipolar DC approach. The substrate can be connected to a radio-frequency (RF) supply, and, if coupled via a serial capacitor (often part of matching RF network), a negative self-bias will occur as a consequence of the small electron-ion mass ratio. In another concept, a bipolar pulsed bias supply can be used with the idea that the positive phase of the bias attract electrons for substrate heating or, in the case of insulating substrates or substrate coatings, to neutralize positive space charge that may have accumulated on the surface during the negative phase of biasing. Bipolar bias techniques are usually asymmetric in voltage, current, and phase duration, and the process can be optimized by selecting these three parameters. In most cases, though, unipolar (negative) pulsed bias is sufficient with the argument that in the bias-off time, the sheath collapses and electrons of the plasma can reach the surface causing surface heating and neutralization of positive charge if accumulated.

The reasoning for biasing is to shift the potential of the substrate with respect to the plasma potential. The resulting difference in substrate and plasma potential determines the fluxes of particles from the plasma to the substrate. For example, by accelerating ions through negative bias one can control their energy with crucial consequences for the net deposition rate (arrival rate minus sputter rate) and structure of the coating.

The potential difference between substrate and plasma drops in a thin space charge layer adjacent to the biased substrate, called the sheath. Negative bias repels plasma electrons and creates a positive space charge layer. There are numerous papers and books on the formation and properties and sheaths, see e.g. [84, 85] and references therein.

Depending on the amplitude of the bias, one may distinguish different effects. At very high bias voltage (many kilovolts), ions are accelerated to kinetic energies that allow them to penetrate deeply under the

surface, a process known as ion implantation. Because no ion source or ion accelerator was involved, but the biased substrate was immersed into the plasma, the process is called Plasma Immersion Ion Implantation or PIII [85]. No coating is obtained unless one introduced condensable vapor or the high bias is switched off, e.g. when using pulsed bias at low duty cycle. The latter case, one has a hybrid implantation (bias on) and deposition (bias off) method, also known as Metal Plasma Immersion Ion Implantation and Deposition or MePIIID [25, 86].

If the high bias voltage is high *and* the duty cycle is high (in the limiting case: DC), more atoms are removed from the surface than ions and atoms arrive. This is the mode of ion etching, an important technique to prepare the substrate for the actual coating. Argon ions are often used for ion etching but metal ions from a cathodic arc can be used as well. Münz and coworkers [30] developed Arc Bond Sputtering (ABS), a coating technology where sputter deposition is preceded by an ion etch step with cathodic arc plasma.

At low or moderate bias we have the regime of net deposition, i.e. coating through subplantation and energetic deposition as discussed before. One should note that the general idea of energetic condensation as facilitated through vapor ionization and substrate bias was invented several times, but most influential was the "ion plating" approach introduced by Mattox in the 1960s [87]. Cathodic arc deposition with bias can be regarded as a version of ion plating.

The section will be concluded by a brief discussion of biasing and substrate arcing. Arcing occurs when the local electrical field strength at the substrate exceeds a threshold value of about 10^6-10^7 V/m. The actual value depends, among other parameters, on the material and surface conditions. Even relatively low bias voltage can lead to arcing because the voltage drops across the sheath, and not across the substrate-wall or substrate-source distance. At the high surface field strength, field emission of electrons from local emission centers can run away, i.e. become unstable due to thermal enhancement of the emission. As a result, electron emission can switch in the explosive mode, as on the arc cathode, with the dense substrate plasma causing an electric short of the sheath. The substrate voltage "breaks down" and high substrate current is observed. Substrate arcing can be avoided or at least minimized by using pulsed bias, lower bias voltage, lower plasma density, or a combination thereof. Additionally, the use of modern bias supplies with fast arc suppression has largely eliminated the problem.

Applications

The vast majority of cathodic arc applications uses reactive deposition of various nitrides and some oxides, and sometimes multilayers. As a rule, macroparticle filters are not used because macroparticles can be tolerated in most applications. These applications include hard and wear-resistant coatings on cutting and forming tools, decorative and corrosion resistant coatings on doorknobs, faucets, showerheads, and other

plumbing and building appliances, metallic shielding coatings against electromagnetic (EM) and radio-frequency (RF) interference, e.g. on the inside of the plastic housing of cell phones, light reflectors, and many others. The most important applications and typical coatings are compiled in Table 1. Table 2 lists selected materials and their most important properties.

It is estimated that the world market for cathodic arc coatings (value added) is about B$1 annually. There are numerous companies offering arc coating equipment and arc coating services. It is impossible to even name all important players, so only examples shall be given without specifically endorsing one or the other. Figure 11 shows an example of a state-of-the-art batch coater for coatings on cutting tools. Loading and unloading is accomplished with pneumatic loading tool. One can see heater elements that bring the tools to the desired temperature before coating starts. The arc sources are equipped with shutters allowing the operator to burn the arcs prior to the actual coating step. Another example of a very large batch coater, shown in figure 12, is made by Hauzer Techno Coating. Such process chambers are also capable of coating large parts.

Most of the commercial coating tools are batch coaters. Figure 13 shows one of the few exceptions, namely an in-line coater, characterized by a sequence of adjacent chambers designed to handle specific process steps such as loading, heating, cleaning, arc coating, cooling, unloading. In-line coaters can have large production throughput, often for large-area substrates. Drawbacks of inline coaters include reliability and maintenance issues and high cost.

Figure 14 shows a cross-section scanning electron microscope (SEM) micrograph of an alloyed TiAlN coating deposited by cathodic arcs at a substrate temperature of about 500°C. The multilayered structure is a consequence of the three fold substrate rotation and periodical switch-on and -off of different sources. The substrate material was WC/Co cemented carbide.

Macroparticles are one, if not *the* major issue in cathodic arc coatings. For instance, the corrosion resistance is compromised when a macroparticle is incorporated in the coating, disrupting the dense, continuous film. Such locations are the weak points subject to corrosion attack. Macroparticles can reduce the shine of a decorative coating; polishing the coatings helps but one would rather prefer to deposit the coating without macroparticles in the first place. There are many motivations for the implementation of macroparticle filters, however, reduced deposition rate, large size and low efficiency, and most importantly increased cost have prevented broad introduction of macroparticle filters in these areas. Nevertheless, first industrial filters have appeared on the market.

Another route of improving coating quality without filters is to affect macroparticle production at cathode spot, i.e. trying to address the issue of generation rather than separation. By operating the cathodic arc

discharge with background gas, as opposed to the vacuum mode, cathode spots tend to be in "type 1" which is characterized by smaller erosion craters and less macroparticle erosion. The application of magnetic fields, driving and steering [50] the apparent arc spot motion, reduces the residence time of a cathode spot, and thus less and smaller macroparticles are produced compared to the non-driven case.

There are a few emerging applications where filtered arc deposition is crucial, for example, the deposition of dense optical films, or ultrathin diamond-like carbon films on magnetic storage media (disks) and read-write heads, or the filling of sub-micron trenches and vias with copper. It will be exciting to see in which areas advanced cathodic arc techniques can make a difference.

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Table 1: Commercial application and typical materials of cathodic arc coatings.

Category	**Application**	**Typical Coating Material**
Hard coatings	Cutting tools	TiN, TiAlN, TiCN, TiAlYN, multilayers
	Forming dies and punches	CrN, multilayers
Hard coatings with solid lubrication layer	Cutting tools	TiAlN/W-C:H; TiAlN/WC/C; TiAlN/MoS_2
	Forming dies and punches	CrN/W-C:H
Decorative and protective coatings	Faucets, shower heads	ZrN, CrN, TiAlN
	Door hardware	ZrN
	Watch housing and wrist bands, jewelry	ZrN, TiN, Au, TiAlN
Functional coatings	engine parts fuel injection automotive interior parts	CrN (pistons) metal-containing DLC metal-containing DLC, AlSn,CrN
	textile machinery	TiCN, metal-containing DLC
	EMI/RFI shielding	Al, Cu, Ni-Cr, with sheet resistance < 1 Ω/
	reflective coatings e.g. for automotive lights	Al, Cr, stainless steel, Ni-Cr
	bio-compatible surfaces for medical tools and implants	Ti, DLC, TiN, TICN, ZrN, and CrN, Ag, Au, Pt
	metallization and diffusion barrier layers for semiconductors	Ta, TaN, Cu
	protection of magnetic disks and read-write heads	ultrathin diamond-like carbon

Table 2: Examples for cathodic arc coatings for tool or decorative applications, with thickness 2-10 µm; data from various sources including web pages of companies offering arc coatings.

Coating material	**color**	**hardness (HV 0.05)**	**maximum working temperature (°C)**	**coefficient of friction**	**most important property and application**
TiN	gold	2300-3200	600	0.65	still most common arc coating due to its hardness, inertness, and color; cutting tools for iron-based materials
TiAlN	bronze, brown	2200-3500	800	0.42	excellent oxidation resistance at high temperature, multilayers for carbide and high-speed tools
AlTiN	grey, black	4100-4800	800	0.42	very high temperature oxidation resistance because produces Al_2O_3 when high temperatures are encountered., higher hardness and smoother surface finish compared to TiAlN; dry machining, machining titanium alloys, inconel, stainless alloys and cast iron.
TiAlN/WC/C		2600/1000	800-1000		high-temperature solid lubrication multilayers, for carbide and high-speed tools
TiCN	pink to dark-gray, black	3000-4400 (softer at high temp)	400-500	0.32-0.45	lower coefficient of friction, high hardness, toughness, and wear resistance; superior to TiN when machining stainless steels, high nickel alloys, cast iron, non-ferrous materials and plastics
TiAlCN	blue-black				decorative
TiO	indigo-black				decorative
CrN	silver-gray	1700-2900	620-700	0.55	excellent corrosion, oxidation resistance and high hardness at high temperature; machining of copper, molding tools
CrC	silver-gray	2300	650		corrosion and oxidation resistance; Al and Mg die casting
ZrN	white-gold	2600-3000	500-600	0.6	high hardness, excellent corrosion resistance, low coefficient of friction; decorative coating, coating for medical and surgical instruments
WC/C	black	1000	300	0.2	low friction in dry cutting

Figure Captions

Figure 1. Illustration in Edison's patent application "Art of plating one material with another," filed on January 28, 1884, granted as U.S. 526,147 in 1894.

Figure 2. Absorption photograph of cathode spot: exposure time 0.4 ns achieved with back-illumination by a pulsed dye laser, from [28].

Figure 3. High-resolution streak camera picture of a cathode spot on titanium, arc discharge current 80 A, with resolution in time and space indicated; photo courtesy of B. Jüttner, Berlin.

Figure 4. Erosion traces on a molybdenum cathode, as seen in an electron microscope. The craters were caused by cathodic vacuum arc discharge in a magnetic field. A magnetic field was present and therefore the erosion craters appear aligned in a chain. One can clearly see two different types of craters, commonly labeled type 1 (small, well-separated) and type 2 (larger, adjacent). Photo courtesy of B. Jüttner, Berlin.

Figure 5. Schematic of macroparticle production at cathode spots, after B. Jüttner, Berlin.

Figure 6. Classic 90°-duct filter, originally developed by Aksenov and coworkers.

Figure 7. Commercial 45°-knee filter offered in the 1990s by Commonwealth Scientific Corporation (Photo courtesy of D. Baldwin, Arlington, VA).

Figure 8. Open S-Filter showing plasma transport along the curved magnetic field and the separation of macroparticles due to their inertia.

Figure 9. 90°-duct filter with rectangular cross section for large-area coatings.

Figure 10. Cathode spot moving along around a rod cathode from left to right in a spiral fashion; arc current 100 A, axial magnetic field ~20 mT, CCD camera with exposure time 16.6 ms. One can see spot splitting or branching and the superposition of steered and random motion.

Figure 11. Modern arc coater for cutting tools (Photo courtesy of Balzers Ltd., Liechtenstein).

Figure 12. Very large batch coater (Photo courtesy of Hauzer Techno Coating, Venlo, The Netherlands).

Figure 13. In-line coater using cathodic arc processing steps; Photo courtesy of Kobelco, Kobe, Japan.

Figure 14. SEM micrograph of a cross section of an alloyed TiAlN coating WC/Co cemented carbide (Photo courtesy of Balzers Ltd., Liechtenstein).

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