Plasma and Ion Sources in Large Area Coatings: A Review

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Abstract
Efficient deposition of high-quality coatings often requires controlled application of excited or ionized particles. These particles are either condensing (film-forming) or assisting by providing energy and momentum to the film growth process, resulting in densification, sputtering/etching, modification of stress, roughness, texture, etc. In this review, the technical means are surveyed enabling large area application of ions and plasmas, with ion energies ranging from a few eV to a few keV. Both semiconductor-type large area (single wafer or batch processing with ~ 1000 cm²) and in-line web and glass-coating-type large area (> 10⁷ m² annually) are considered. Characteristics and differences between plasma and ion sources are explained. The latter include gridded and gridless sources. Many examples are given, including sources based on DC, RF, and microwave discharges, some with special geometries like hollow cathodes and \( E \times B \) configurations.
1. Introduction

The development of ion and plasma assisted deposition processes can be traced back many decades [1]. The effects of ions, electrons, and other energetic particles are now widely utilized for substrate cleaning as well as to assist and control film growth. Some of the particles are not just assisting but they may condense and thereby become part of the growing film or structure. Depending on the coating process, a wide range of particle species and energies can be involved.

Large area coating presents additional challenges for the broad use of plasma and ion sources, which are due to cost, limited uniformity, high gas consumption, limited flexibility with available hardware, etc. On the other hand, an increasing number of modern applications depend heavily on the use of large area plasma or ion assistance.

It should be mentioned that “large area” has quite different meanings for different applications. In the semiconductor world, large area refers to processing of wafers of 300 mm diameter or larger [2]. Somewhat larger areas, say (0.5 m)^2, are expected by manufacturers of flat panel displays, solar cells, and organic light-emitting diodes (OLEDs). The ultimate “large area” is realized by in-line web and glass coaters: It is not unusual to have an in-line coating width of up to 3.6 m and with an annual coated area exceeding 10^7 m^2 [3].

The terms low-density and high-density plasma will be mentioned. It is common [4] to consider plasma densities of 10^9-10^10 cm^-3 as low, while high density implies 10^{11}-10^{12} cm^-3. Plasma densities of 10^{13} cm^-3 or higher are rarely achieved. High and very high density plasmas require high concentration of energy and as a result they tend to be non-uniform. Large area treatment is only possible in conjunction with substrate motion.

The review starts by looking at a number of particle-induced effects because they form the basis for the selection of hardware components and process parameters. A distinction between plasma and ion sources will be made. The focus shifts then to large area treatment and explains plasma generation principles, ion extraction (if applicable), and source embodiments. Special cases like plasma immersion treatment are also briefly mentioned.

2. Effects of plasma and ion treatment

There are numerous papers [5-11] and textbooks [12-15] on plasma and ion effects and therefore a few notes should suffice here. Emphasis is put on physical vapor deposition (PVD) techniques, although some selected, plasma-enhanced chemical vapor deposition (CVD) will also be mentioned.

In coating processes without plasma assistance, the mode of nucleation and film growth is mainly determined by the thermochemistry of the substrate and film materials and the temperature of the system. Additionally, the rate of deposition, film thickness, and angle of incident are important [16]. These processes lead to island (Volmer-Weber), or layer-by-layer (Frank-van der Merve), or mixed layer-island (Stranski-Krastanov) growth. The effect of temperature on microstructure can be illustrated by structural zone diagrams [16, 17]. By the addition of plasma and ion assistance, or energetic condensation, films can grow far from thermodynamic equilibrium. In the simplest case, considering sputtering, Thornton [18] developed his well-known structural zone diagram that includes a pressure axis: pressure is an indirect measure for the energy of assisting argon ions.
Incident ions provide additional energy to surface atoms, which effectively leads to higher surface mobility, thereby aiding surface atoms to find energetically preferred locations. Ion beams can promote the formation of textured films [19] and texture alignment [20]. Recently, special interest is in low energy ions, i.e., ions of hyperthermal energy yet still low enough to not cause ion damage. In absolute units, this is the range of about 1-30 eV. Low energy treatment is sufficient to remove (desorb) weakly bounded surface atoms, especially water that is always present unless the process is done at very high temperature or in ultra-high vacuum (UHV). Theoretical modeling of ion effects on densification and texture evolution needs to take into account thermodynamic properties and stress and strain energies [21, 22].

In the case of polymer substrates, energetic ions promote “functionalization,” e.g. the activation of C=O functional groups that can lead to well-adhesive films by forming strong covalent bonds such as Al-O-C in aluminum metallization [23].

At somewhat higher energies, up to a few 100 eV, shallow implantation (subplantation) will occur, often associated with film densification, increased hardness and Young’s modulus, high compressive stress, reduced roughness, and with high diamond bond (sp³) content in the case of amorphous carbon. At the high end of this range (200 eV and greater), secondary electron emission and sputtering starts playing an important role. Ion bombardment of crystalline films will cause heavy ion damage and in extreme case full amorphization [24] for some materials and texture changes for others [20].

At even higher energies, >500 eV, the rate of sputtering of the surface will exceed the rate of deposition, effectively prohibiting film growth. This range can be characterized as an etch mode, which is important for surface preparation and patterning processes. In the case of polymer substrates, ions of too high energy and/or too high dose lead to substrate damage by chain-scissoring [23].

Particle energies of a few keV are used to remove material and to produce shallow implant profiles, which is important to some semiconductor processing. Another example of a process in this energy range is plasma nitriding, where hard and inert nitride phases are formed in the near-surface region of steel or aluminum alloys [25].

Finally, at the very high end of the ion energy scale, ion implantation at 100s of keV or some MeV is done routinely, but these processes and applications are beyond the scope of this review and not to be further considered.

Apart from ion bombardment, plasmas also offer utilization of their electron component, which is especially useful when positive charge on an insulating surface needs to be neutralized, or when the growing film needs to be heated without heating the bulk of the substrate.

3. Classification of ion and plasma sources

Source can be classified by their species, e.g., noble or reactive gases, molecular, decomposing precursor gases, and metals (condensable). Another way of creating a systematic scheme is to look at the mechanisms of plasma generation, which mainly includes capacitive and inductive radio-frequency (RF) coupling, microwave, electron-cyclotron resonance (ECR) and helicon plasma, hollow cathode, constricted glow, plasma of sputter magnetron, possibly enhanced by pulsing, post-ionized vapor sources, and cathodic arc plasmas. In all of these sources, the common theme is that atoms or
molecules are ionized by electrons, and electrons must be given sufficient energy to enable ionizing collisions. The various forms of plasma sources embody different means of giving electrons energy for ionization.

There is sometimes confusion on the terms ion and plasma source. In the simplest case, one can think of an ion source as a plasma source combined with an ion extraction system. The plasma is an ensemble of ions and electrons and neutrals, which is quasi-neutral. During extraction, ions transition through a sheath region between extraction electrodes. The sheath’s high electric field accelerates ions to a kinetic energy given by the sheath voltage times ion charge state. Large area ion extraction is commonly done via multi-aperture three-grid system of the acceleration-deceleration type [26], and such ion sources are known as “gridded” ion sources (Fig. 1).

Gridded ion sources offer the advantage of tightly controlled ion energy and dose but are not suitable to low energy due to space charge limitation of current density. For the large area work considered here, ion extraction is done either by a multi-aperture grid or multi-slit system. The characteristic size (hole diameter or slit width, respectively) must be smaller than the sheath thickness at the given extraction voltage and plasma density, otherwise the plasma will flow into the extraction gap and shorten it (the extraction voltage will “break down”).

Most ion sources of high energy (1 keV and greater) are gridded sources. The have a fundamental current limitation due to space charge in the extraction system. In planar geometry, the maximum current density is given by the Child equation [15, 26]

\[ j = \chi \frac{V}{d^2} \]

where \( \chi \) is a material-specific constant, containing the charge state number \( Q \) and mass \( m \), \( \varepsilon_0 \) is the permittivity of free space, \( e \) is the elementary charge, \( V \) is the extraction voltage and \( d \) is the distance between extraction electrodes, or equivalently, the sheath thickness.

After extraction, the space charge of the ion beam attracts free electrons that are provided by a space charge neutralizer or generated by collisions with the residual gas, substrate, chamber wall, or other components. The ion beam quickly becomes space charge compensated, and only in the fully compensated state it will propagate in a near parallel beam fashion. Without space charge compensation, the ion beam will “blow up” and rapidly lose its original current density. The main difference between quasi-neutral plasma and the fully space-charge-compensated ion beam is the strong directed beam component in the ion velocity distribution function.

Space charge limitation represents a fundamental problem when low energy but high current sources are required. One possible approach is to utilize a four-grid system in which the last two grids are used to decelerate ions in a controlled manner.

A more common way to circumvent current limitation is utilizing ion acceleration that is not based on extraction. This is possible by generation of electric fields in magnetized plasmas. With magnetized one usually means that the motion of plasma electrons is governed by the magnetic field, i.e. electron gyrate around magnetic field lines, which greatly impedes their mobility perpendicular to the magnetic field lines, while the longitudinal mobility is not affected. Under these conditions, each magnetic field line is approximately an electric equipotential line. The electric potential can be different going from magnetic field line to field line, hence an electric field can exist,
which can be used for ion acceleration. One should note that the magnetic field strength is usually not strong enough to also magnetize ions, i.e. the ion gyration radius is large compared to the system size. Electric and magnetic field are essentially perpendicular, causing $\mathbf{E} \times \mathbf{B}$ drift. The drift path can be closed, leading the closed-drift sources. An example for “gridless” ion source is the closed-drift anode-layer source, whose design will be mentioned later.

At the low end of the energy scale, in the range < 50 eV, the difference between plasma source and ion source becomes less pronounced, or may not be existent, especially when the plasma source generates a fast drifting plasma. For example, the streaming plasma from a cathodic arc plasma source may be considered as a high-current, low energy ion beam with a broad ion energy distribution function [27].

4. Source geometry: large area, linear, and arrays

In order to achieve large area treatment, one may use a source whose output area is comparable to or even larger than the substrate area. This can only be done in “large area” coating in the semiconductor sense, where, for example, multi-aperture gridded ion sources can be used. Substrate motion is common to improve uniformity. Substrate motion is a prerequisite to large area web and glass coating. In these applications, linear sources are used. The substrate is moved perpendicular to the linear source direction. The length of a linear source should somewhat exceed the width of the substrate in order to reduce non-uniformity near substrate edges.

While linear sources are common, some source designs are more suitable as point sources or short-slit sources. In these cases, one can approach large area processing by assembling an array of sources (e.g. [28]). This has the additional advantage that the individual components of the array can be individually controlled to obtain better uniformity [29]. Process parameters should be monitored with spatial and temporal resolution, providing signals for feedback loops to control gas flow distribution, power distribution, pumping speed adjustments etc. For example, plasma optical emission monitoring is suitable tool for plasma feedback tuning [30, 31], enabling optimized film properties, such as low resistivity and high transmittance of indium tin oxide (ITO) [32].

5. Large area ion sources

5.1 Large area filament source

One of the simplest ways of producing relatively dense plasma is to utilize a thermionic arc fed by electrons from one or more hot filaments. A well-known design is the Kaufman source [33], where plasma is produced by a filament or RF discharge. The plasma density can be enhanced by confining electrons in a magnetic multipole “bucket” – ion source technology originally developed magnetic fusion [34, 35]. For ion doping in large area LCD (liquid crystal display) fabrication, Naito and coworkers [36] used thermionic arc plasma of diborane and phosphine fed by three independently controlled hot filaments (Fig. 2). This system is an example for a four-grid ion extraction and deceleration. A beam profile monitor was used to provide feedback to the hot filaments, which resulted in better than 5% beam uniformity along the 600 mm ion beam.

Filament-based plasmas have severe limitations in reactive gases due to short filament lifetime and plasma contamination. Additionally, the thermal load caused by hot filaments can be detrimental to sources and substrates.
5.2. Capacitively and inductively coupled RF sources

RF power can be coupled to the discharge volume capacitively or inductively (Fig. 3) [2, 37]. Capacitively coupled sources can easily generate plasma of low density filling large volume. Inductively coupled sources can be seen as a transformer system, where the plasma itself represents the secondary. Most RF sources work at the standard frequency of 13.56 MHz. Relatively higher plasma densities can be obtained from a capacitively coupled source when higher frequencies are used (e.g. VHF, up to 300 MHz [38]). For the fabrication of large ULSI semiconductor devices by ion implantation, Tanjyo and coworkers [39, 40] increased the RF frequency to 500 MHz (UHV frequency region) in a large area ribbon beam source, 300 mm x 600 mm, equipped with a magnetic cups plasma container and multi-aperture ion extraction system (Fig. 4). In large area system, special measures are needed to obtain uniform plasma, in particular, RF power absorption needs to be well distributed. In the above work, this was achieved by supplying the RF to several RF wave entrances, leading to 2% variation in longitudinal ion current for a beam.

5.3. Large-area vacuum-arc ion source

Mass-selected ion implantation of dopants is usually done at very low ion current (µA); large areas (in the wafer sense) are obtained by ion beam scanning. The large-area filament or RF-based ion sources mentioned above are exceptions in that neither mass selection nor scanning was employed. Another example of a broad beam ion source is the vacuum arc ion source, also known as “MEVVA” (metal vapor vacuum arc) ion source [41]. Here, the ion species are determined by the cathode material rather than a working gas. In its largest embodiment, a beam diameter of 500 mm was realized [42], though the beam was not uniform but Gaussian.

6. Large area gridless ion and plasma sources

In contrast to the ion sources of the previous section, the sources described here do not have a grid extraction system. There are essentially plasma generators, and some have means of (gridless) ion acceleration. The classification used here is based on plasma generation principle and geometry.

6.1 Linear Magnetrons

Most large area coaters use magnetrons for sputter deposition (Fig. 5). Linear magnetrons can be designed as planar (stationary) single or dual cathodes or with rotatable target tubes (cylindrical magnetron). The principle is the same as with smaller size (circular) magnetrons but the shape of the erosion “racetrack” is elongated to arbitrary length, e.g. up to 3.75 m to accommodate the 3.6 m width of glass sheet in large in-line coaters [43]. Although magnetrons are primarily designed to deliver sputtered target material, the plasma generated can be (“parasitically”) used to assist in film growth. Particle bombardment can intentionally be enhanced by unbalancing the magnetic field [44]. Rossnagel [45] measured 2% - 50% of arriving particles are energetic, the specifics depending on the gas and target material.

As shown in Fig. 5, positive ions are accelerated towards the target and away from the substrate, and therefore the sputter magnetron geometry is generally not well
suited as an ion source. Furthermore, sputtering and plasma properties are coupled. Besides introducing magnet imbalance, relatively little explicit use has been made of a magnetron as a generator for plasma assistance. New opportunities may arise with the availability of modern mid-frequency [46, 47] and pulsed power supplies [48, 49]. They extend the possibilities to change the plasma properties beyond what could be done with DC and RF supplies. The plasma of a magnetron is highly non-uniform: the plasma density falls rapidly with distance from the target, and therefore any plasma effect strongly depends on the target-to-substrate distance. Along the length of the magnetron, uniformity can be excellent but end-effects need to be taken into account, as with all linear sources.

6.2 Linear Magnetrons with negative ion acceleration

A special case of ion assistance with a conventional magnetron configuration is when negative ions are involved. For example, F, Cl, and O form negative ions. In reactive magnetron deposition where these elements are present in the target or sputter gas, the growing film is bombarded by the corresponding negative ions.

The idea of negative ion assistance can be extended to other sputter materials by cesiating the target surface. Cesiation is a well-developed technique for negative ion sources [50], first explored in the late 1960s [51]. Cesium atoms on the target surface lower the potential barrier and increase the tunneling probability of electrons, thereby promoting formation of negative ions of sputtered atoms [52, 53]. Magnetron-based negative ion-assisted large-area deposition was demonstrated for the deposition of indium tin oxide (ITO), SiO₂, and copper metallization [54].

6.3 Linear sources of end-Hall and anode-layer type

The magnetron concept can be reversed such as to accelerate positive ions away from the source (Fig. 7). As with the magnetron, ion acceleration is accomplished by an electric field enabled by the presence of a magnetic field. As a result of crossed electric and magnetic fields, a circulating electron current is generated. Gridless ion sources are not subject to space charge current limitation, as mentioned before. Though, space charge can exist and may need to be minimized by filament or RF plasma neutralizers. There are two basic ion source geometries, commonly called end-Hall and closed-drift anode-layer design. Both originated from research in electric space propulsion, which was pioneered in the former Soviet Union [55] and later adopted for industrial use by Kaufman and co-workers [28, 33, 56] and others [57-59].

In the end-Hall design (Fig. 6), the ion beam leaves the source at the end axis of the magnetic field, hence the name. Circular end-Hall sources have been arranged to form a modular linear source [28] and also a linear version (dubbed “magnetic mirror source”) was developed for large area plasma treatment [60, 61]. More commonly used for large area surface treatment is the closed-drift design (Fig. 8), which can readily be scaled to any desired length [59]. The ion energy spread is large because the accelerating potential difference depends on the ion production location. The source is well suited when energetic beams of > 100 eV are needed and when large beam divergence, large energy spread, and some amount of sputtered cathode material can be accepted. Due to its simplicity and robustness, the anode-layer source has become a popular source for large
area web and glass treatment. For many applications, though, sputtered cathode material represents unacceptable contamination.

6.4 Linear Constricted Glow and Constricted Magnetron Discharge

Glow discharge plasma can be enhanced by a potential double layer that is formed when the discharge path is constricted by an orifice (nozzle). Electrons are accelerated by the double layer’s electric potential drop, which can easily exceed the ionization energy of the gas atoms or molecules [62]. In this way, an electron-beam-enhanced plasma is produced at the orifice and flowing to the substrate [63]. Although the anode can be remote and planar, a common approach is to place an annular (hollow) anode right downstream of the orifice, leading to devices termed hollow anode ion, electron, or plasma sources [64-66].

Fig. 9 shows an array of 10 discharge cells, forming a quasi-linear Constricted Plasma Source that can be scaled to arbitrary length [67]. This type of source is characterized by low ion energy (< 20 eV) [68].

A magnetic field can be added [65, 66], as to magnetically insulate the anode, thereby creating an \( \mathbf{E} \times \mathbf{B} \) field and Hall current, which enhances the plasma density at the nozzle (Fig. 10). One may consider this configuration as a constricted magnetron discharge. Recently, more powerful versions of a more or less constricted magnetron discharge were developed for plasma-assisted deposition of oxide films [69].

6.5 Linear hollow cathode arc

Hollow cathode discharges are known to produce plasmas of high density. The hollow cathode effect is observed when opposing cathode sheaths cause electrons to be reflected multiple times, thereby effectively reducing electron losses and greatly increasing the ionization probability of the gas or vapor. For large areas, the hollow cathode effect can be obtained by using parallel plates forming a linear source. The hollow cathode can be operated in glow or arc modes, depending on the electron emission mechanism and gas/vapor supply. Bardoš and coworkers [70, 71] have developed a linear arc discharge (LAD) based on a RF-generated hollow cathode discharge between two parallel plates (Fig. 11). It is a form of an arc discharge because electrons are emitted via thermionic emission mechanism. A magnetic field perpendicular to the plates promotes the reflection motion of electrons, enhances ionization and thereby ion bombardment and heating of the cathode plates. The chamber represents the anode. This source has been used to assist in the deposition of hard, high temperature compounds, such as TiN; it is less suitable for web coatings due to its high operational temperature.

6.6 Capacitively coupled plasma sources

Another example of a linear, RF-power plasma source was developed by Rank and coworkers [72]. The power is capacitively coupled, which allowed them to place the counter electrode behind the substrate (Fig. 12). Such configuration is well suited for thin substrates such as a plastic foil (web). Web treatment at very high speed (\( v_{\text{web}} > 3 \) m/s) has been demonstrated. A weak magnetic field (\( \sim 10 \) mT) is used to enhance the plasma near the substrate and increase ion flux to the web. Such plasma has excellent properties to treat (clean, functionalize) polymer surfaces.
In order to increase plasma density and associated deposition or etch rates (depending on gas and process), frequencies higher than 13.56 MHz have been used. However, issues of non-uniformity are more evident because the wavelength is comparable to characteristic dimensions of the system or substrate: standing and evanescent waves appear. Rüdiger and coworkers [73] developed a source operating at 81.36 MHz to be used with silane for the deposition of microcrystalline silicon films with uniformity better than 5%. Its design (Fig. 13) is similar to Rank’s source for web treatment (Fig. 12).

6.7 Inductively coupled plasma sources

While most large area RF sources are capacitively coupled, there are also examples of inductively coupled sources and source arrays. Wu and Lieberman [74], for example, developed an inductively coupled large area (71 cm x 61 cm) plasma source driven by a 13.56 MHz traveling wave (Fig. 14). Launching a traveling wave eliminates the standing wave effects that impede uniform plasma treatment. Improved performance of the same system to plasma etching was found when a Penning gas mixture was used: metastable argon enhanced oxygen dissociation and increased the plasma density, compared to pure oxygen plasma [75].

Park and coworkers [76] opted to arrange a 2x2 array of inductively coupled plasma (ICP) sources, each having its own planar, circular antenna and quartz window. In this way they obtained oxygen plasma for uniformly processing 32 cm x 40 cm glass plates as part as flat panel fabrication.

Tuszewski and coworkers [77] compared external and reentrant inductively coupled sources and determined that the reentrant design was superior to obtain large area plasma for plasma immersion processing (cf. point 8 below).

6.8 Microwave plasma sources

Microwave plasma sources are less common for large area processing than RF plasma sources because it is more difficult to produce uniform large area plasma. However, microwave power is very efficient in generating plasma and chemically active species, and one can use readily available, low-cost 2.45 GHz microwave generators and industrially established methods of microwave guiding. Typical gas pressures are 10 Pa and higher. Lower pressures require the application of a magnetic field. Especially efficient are system with electron cyclotron resonance (ECR), where the electron gyration frequency is equal to the microwave frequency. High (near atmospheric) pressure microwave plasma sources are discussed in a later section.

Microwave discharges can be distinguished by the type of microwave field applicator or wave launcher used to excite a given propagation mode [78, 79]. The design of the applicator usually depends on the characteristics of the wave to be excited considering excitation frequency, kind and pressure of gas, plasma density, presence or absence of an external magnetic field, and boundary conditions. Absorption of microwave power by electrons can be either collisional or resonant. The collisional case has a lower limit to the operating pressure. In the case of resonant absorption, namely Landau damping, Čerenkov absorption, or cyclotron absorption, power transfer is the highest in the low pressure range, typically less than 1 Pa.

Zakrzewski and Moisan [80] distinguished transmission-line applicators and
antenna applicators. In the first case, the plasma itself constitutes an essential support for the propagation of the wave. It requires a minimum plasma density. In the case of antenna-type applicators, the wave is considered to radiate from the applicator. Some systems that can be operated in either "antenna" or "transmission-line" mode. The transition from one mode to the other depends on the density of absorbed power in the plasma. At a given frequency, the highest plasma density is obtained with a "transmission-line" system.

An example of a linear microwave plasma source of the transmission line type is the “Duo-Plasmaline” [81, 82]. In this design, a copper rod is placed inside a quartz tube: it represented the inner conductor, and plasma forming in the low pressure gas (5-500 Pa) outside the quartz tube represented the outer conductor. The plasma source was extended by a second, parallel copper-quartz tube, producing uniform plasma over region of 10 cm x 50 cm. Large area oxygen treatment was demonstrated by moving a sample stage across this linear source.

Examples of the antenna type sources are slot antenna (SLAN) sources (see review [83]). A surface wave source with an annular slot was shown to produce dense plasma with a diameter of up to 30 cm (Fig. 15) [84, 85]. A second generation, larger source (SLAN II) was designed with an annular cavity and multiple slots (Fig. 16).

A tunable surface wave cavity source for plasma areas exceeding 50 cm x 25 cm was developed by Wu and coworkers [86]. Better than 10% uniformity was achieved by tuning a 12-period vane type slow wave structure. Yamauchi and coworkers [87] looked for a large-area design that avoids the usual large dielectric plate; they injected microwaves through slots in a metal plate structure that had periodic grooves, giving plasma density in the $10^{11}$-$10^{12}$ cm$^{-3}$ range.

Plasma density can be further increased by using the electron cyclotron resonance (ECR). For large area processing, distributed ECR (or DECR) sources have been developed [88]. Electrons are accelerated by the microwave electric field and distributed close to a multipolar magnetic field structure, which is commonly produced by set of permanent magnets strong enough to provide ECR condition. The ensuing fast electrons are trapped in the multipolar magnetic field and drift along the magnets. Closed magnetic configurations are used to avoid electron losses at the boundaries of the confinement structure. For example, a 24-antenna DECR-source has been used to deposit Ge-doped silica by CVD of silane on 40 cm x 40 cm substrates [89].

6.9 Electron-beam-generated plasma sheet

There have been two basic configurations to generate large-area plasma sheets by using energetic electron beams. In one configuration, developed in Tomsk, Russia, a rectangular hollow cathode plasma is the feedstock from which electrons (not ions) are extracted [90-92] (Fig. 17). Electrons are accelerated to a desired energy, typically 1-6 keV, and injected into a region of moderate gas pressure (1-5 Pa), where electron-ion collisions lead gas ionization and the formation of a “plasma ribbon.”

Independently, a similar concept was pursued at the Naval Research Laboratory [93, 94]. In contrast to the Tomsk setup, electron acceleration is governed by the cathode fall voltage (i.e., not tunable independently of the plasma production), and the electron beam is guided along an extended longitudinal magnetic field. The magnetic field promotes ionization and determined the position of the gas ionization zone (Fig.18). In
both systems, and in contrast to other linear plasma sources, the plasma is produced as an extended sheet parallel to the surface of the substrate. To enhance ion treatment of the substrate, a bias voltage can be applied to the substrate or substrate support plate; Manheimer and coworkers [95] considered the special case of RF bias in the presence of a magnetic field for this geometry.

7. Large area plasma at atmospheric or near-atmospheric pressure

7.1 Dielectric barrier discharge

In recent years, plasma processing at atmospheric and near-atmospheric pressure has become a hot topic because of the potential of fast and efficient fabrication without expensive vacuum equipment. Only a few examples of this development can be mentioned here. A major issue of atmospheric pressure processing is insufficient uniformity because the plasma has the tendency of filamentation and to transition into an arc discharge.

The use of dielectric barriers on electrodes is one of the main approaches. Dielectric-barrier discharges (silent discharges) produce non-equilibrium plasma between electrodes covered with dielectric barrier (Fig. 19). An alternating voltage is applied generating an electric field in the gap between dielectrics until discharge (breakdown) occurs. The discharge current is limited due to the presence of dielectric barriers, and the glow discharge does not transit into arc. The preferred frequency is between 1 kHz and 10 MHz, and the preferred pressure between 10 kPa and 500 kPa. Barrier discharges can be scaled from small laboratory reactors to large industrial installations of megawatt power [96].

For most applications, the goal is to avoid plasma filamentation. To obtain homogenous plasma, electrons and metastable atoms should be present before breakdown occurs, for example they have been generated in previous discharge cycle, or they are produced by associative ionization and excitation [97, 98]. Filamentation of the plasma can lead to densely arranged, self-organized structures [99] and is not necessarily an obstacle to uniform area treatment, especially when the substrate is moved.

There are many applications of dielectric barrier discharges (review [96]). The presence of dielectric barriers suggests surface treatment and deposition on dielectrics using plasma-assisted chemical vapor deposition in the atmospheric glow plasma [100, 101]. Barrier discharges are suitable to modify surfaces of polymers like polypropylene, leading to increase in surface energy and wettability [102, 103].

7.2 RF sources

Dielectric barrier structures can be modified and also be used at higher frequencies such as the standard RF frequency of 13.56 MHz. Recently, Yuon Moon and coworkers [104] used a 20 cm long test device (Fig. 20) and reported about a 60 cm scale up. The air-argon plasma was free of filaments with uniformity better than 93%.

7.3 Micro discharge arrays

Micro-hollow cathode discharges are direct current, high-pressure plasmas formed between a cathode with a pin-hole and an anode of arbitrary shape separated by a thin layer of a dielectric material [105, 106]. It is known that many gas discharge parameters scale as the product of pressure and characteristic length, $pd$, and therefore high pressure
operation leads to very small scale. For atmospheric pressure, the typical scale length is 100 µm and smaller. For large area treatment of substrates, arrays of many parallel-operating micro-discharges are being considered [106-108]. These systems can operate in DC or pulsed mode [105].

RF plasma excitation has been used to power an array of hollow cathodes. Baránková and Bardoš [109] used 900 hollow cathodes, with inner diameter of 400 µm each, to obtain a fused hollow cathode (FHC) system for atmospheric pressure processing.

8. Plasma Immersion Techniques

Plasma Immersion Ion Implantation (PIII) is a large-area processing technique based on the formation of a high-voltage sheath between plasma and biased substrate [15]. It was originally developed as a conformal ion implantation technique to synthesize hard and chemically inert nitride phases on the surface of steel and aluminum components, such as engine parts [25, 110]. The technique was expanded to other applications, e.g., shallow p-n junctions were fabricated by ion implantation into semiconductors. An implantation-deposition hybrid technique was developed by adding film deposition [111, 112]. Plasma immersion techniques require the production of a large-volume or large area plasma and application of (usually pulsed) bias to the substrate or substrate holder. Most of the previously mentioned plasma sources are well suited to also serve in plasma immersion processing. In a few cases, the plasma is produced (or at least supported) by the bias supply. For example, fluorine and boron doped hydrogenated amorphous carbon was deposited by pulsed glow discharge CVD [113]. Plasma immersion techniques are increasingly used to control intrinsic stress and texture in films [22, 114].

9. Pulsed power in large area systems

The application of pulsed power to plasma and ion beam production has the advantage that additional process control parameters become available, and that new plasma states can be obtained, enabling exploration of new surface treatments. Pulsed power increases the momentary plasma density, temperature, and enhanced excitation, dissociation and the formation of multiply charged ions, which in turn can obtain high energy via extraction or acceleration in sheaths of biased substrates. The average power can be maintained, and therefore the requirements to power supply and cooling are comparable to conventional DC, CW, or RF equipment (though, most high power pulsed equipment comes at additional cost). A thorough consideration of these effects and equipment is beyond the scope of this review.

10. Energetic Condensation

This review is concluded with a brief look at energetic condensation, i.e. deposition process in which the condensing species themselves have hyperthermal or greater energy, as opposed to a process that is assisted by energetic particles from a noble gas plasma (often argon ions). Energetic condensation is a common process for the deposition of hard and dense films [11, 115-117]. The kinetic energy of the condensing species is generally provided and controlled by the application of bias to the substrate. In the case of pulsed bias and relatively high voltage, energetic condensation becomes a
plasma immersion process, mentioned in section 8. To be effective, the degree of ionization of the condensing species should be high. Filtered cathodic arc plasmas are fully ionized and hence of great interest [112]. Similarly, plasma obtained in ionized sputtering [118] and high power pulsed sputtering contain high concentration of condensable ions.

Focusing on large area cathodic arc deposition, one has to note that the arc plasma is produced at cathode spots, that is, the plasma comes from point sources must be expanded and distributed to be suitable for large area coating. Traditionally, large area arc coating is done using either an array of cathodic arc sources or using large planar or cylindrical cathodes in conjunction with magnetic or electric arc cathode spot steering (steered arc) [119, 120]. Recent development addressed the particle issue in large area coatings by introducing dual filter arrangements for batch coating [121] and linear filters with rectangular cross section for in-line coating systems [122, 123] (Fig. 21).

Energetic condensation is not limited to arc plasmas or ionized metals in sputter plasmas. Ion plating is one form of energetic condensation; it was originally developed by Mattox [124] and has become a high rate process for large areas, in particular processes like “hollow-cathode-activated deposition” [125] and thermionic rod-cathode-activated deposition [126]. In essence, condensable (neutral) vapor is produced in these processes, which is ionized by electrons produced in a high-current auxiliary discharge.

11. Summary and Conclusions

Plasma and ion treatment of substrates is widespread in large area deposition. It is a crucial element to achieve good film adhesion, high deposition rate, and desired texture, stress, surface roughness, and other film properties. Depending on the application, different energies are required, ranging from many keV for ion implantation to a few eV, for film growth assistance. The lower range has become increasingly relevant in recent years because this is the range where ion damage can be avoided though texture and other properties can be affected. The survey presented here focused on the technical means to generate plasmas. Most systems for film assistance do not have ion extraction systems because (gridded) extraction systems are fundamentally limited by space charge (Child law). Therefore, much research and development went into gridless ion and plasma sources. Based on the number of published papers, a large body of work deals with RF and microwave sources, both in the low pressure (vacuum) processing regime as well as the high (up to atmospheric) pressure regime. Obviously, the latter is very attractive although vacuum processing has matured and is not going to be replaced in the foreseeable future. Improved in-situ diagnostics and feedback loops will further enhance the capabilities of plasma-assisted and plasma-based deposition.

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References


Figure Captions

Fig. 1 Schematic illustration of the plasma and ion source relation: ion (beam) sources are generally comprised of a plasma source (plasma generator) and an ion extraction system.

Fig. 2 Example of a multi-filament thermionic arc plasma generator and four-grid ion extraction; a beam profile monitor provides feedback to filaments (adapted from [36]).

Fig. 3 Schematic presentation of RF ion sources. Left: inductively coupled, RF is provided to a coil antenna, inducing RF current in plasma (secondary); Right: capacitively coupled, RF is provided to an electrode antenna, heating electrons in sheath and plasma volume.

Fig. 4 Example of RF ion source, operating at 500 MHz, with four-grid ion extraction from a 600 mm x 300 mm plasma chamber (adapted from [39]).

Fig. 5 Schematic cross section of balanced magnetron: the cathode is the target: it bombarded by ions that are mainly produced by electron-gas collisions. A non-uniform, relatively dense plasma is formed above the target. Ions are accelerated by the electric field as shown on the left side of the figure, leading to sputtering.

Fig. 6 Schematic of an end-Hall ion source, here with a cathode presented as a hot filament. In principle, the electron source can also be a hollow cathode or a plasma-filled RF cavity (adapted from [33]).

Fig. 7 Equipotential lines in the anode-cathode region of a anode-layer ion source (number represent Volts, calculated without taking plasma into account): most of the voltage drops inside the source but a significant drop is seen by ions, accelerating them away from the source (adapted from [58]).

Fig. 8 Cross section of closed-drift anode-layer ion source. The iron frame is a magnetic flux conductor, maximizing the B-field in the plasma region. The cathode is usually grounded and the anode is positive. For details see Fig. 7.

Fig. 9 Array of 10 constricted plasma sources, forming a quasi-linear source of flowing oxygen plasma; array length about 25 cm (from [67]).

Fig. 10 Constricted glow (magnetron) discharge (adapted from [29]).

Fig. 11 Linear arc discharge (LAD) based on a RF-generated hollow cathode discharge between two parallel plates (adapted from [70]).

Fig. 12 Linear capacitively coupled RF plasma source for plasma treatment of high-speed (> 3 m/s) webs (adapted from [72]).

Fig. 13 Linear VHF plasma source for plasma-assisted CVD of microcrystalline silicon (adapted from [73]).

Fig. 14 Coil system of a traveling wave-driven, inductively coupled large area plasma source (adapted from [74]).

Fig. 15 Cross section of an annular slot-antenna microwave source, here with tuner cavities and T-junction tuning (adapted from [85]).

Fig. 16 SLAN II large-area plasma source, featuring a annular wave cavity with slot antenna, capable of producing high density plasma in a chamber of 67 cm diameter (adapted from [127]).

Fig. 17 Hollow cathode electron beam source used to generate a “ribbon” of gas plasma (adapted from [90]).
Fig. 18  Schematic of the large area plasma processing system (LAAPS) of the Naval Research Laboratory: electrons are accelerated when leaving the hollow cathode; they are guided by a longitudinal magnetic field and collide with gas molecules, forming a plasma sheet next to the substrate surface.

Fig. 19  Dielectric barrier discharge at atmospheric pressure for large area surface treatment (adapted from [101]).

Fig. 20  Dielectric barrier plasma source operated at 13.56 MHz in air (adapted from [104]).

Fig. 21  In-lines coating system with linear cathodic arc source and rectangular macroparticle filter (adapted from [123]).
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