It is perhaps surprising that, after the early interest in the process, there was little increase in its industrial take-up until the mid to late 1970’s and the early 1980’s, when some key developments occurred, principally in the USA and Japan, which set the scene not only for wider-scale industrial processing but also for significant improvements in process understanding. This “Second Wave” in plasma-assisted PVD saw a rapid rise in publications output and a growth in the number and size of related conferences. In more recent years there has been a “Third Wave” of activity, which can be linked to specific system configurations and to power supply developments. This is currently being followed by a “Fourth Wave”, led by further hardware and software developments and process breakthroughs. The “waves” of intensive development following Mattox’s first findings are summarized below:

**The 4 Waves of Plasma Assisted PVD Development**

- **The First Wave: DC diode Ion Plating.** Metallic coatings to provide protection.
- **The Second Wave: Enhanced Plasma Systems.** Ionization enhancing additions to the diode layout. Development of a wider range of coatings, including ceramics.
- **The Third Wave: Further ion and vapour source developments.** Additional ionizing systems to further optimize processes, especially for sputtering. Development of further multi-component, layered, nanocomposite and duplex coating systems.
- **The Fourth Wave: Further hardware and control software developments.** Will include: Improved process monitoring and control, including developments to meet the coating needs of specific products and applications (including high volume continuous/semi-continuous and batch processing).

2. The Second Wave

2.1 The Move Away from the Diode Layout

Following the first wave in PAPVD, which tended to utilize a DC diode system layout, and (usually) resistive evaporation, the second wave was driven by a desire to deposit ceramic phase coatings. It became evident that these coatings needed higher ionization levels than the simple DC diode could provide. With the move to ceramic coating came a need for a higher temperature evaporation method such as electron beam PVD. A key innovator was Bunshah [6, 7] who developed a technique called Activated Reactive Evaporation (ARE), which involved the use of a supplementary anode in the deposition chamber (but no substrate bias). He argued that the anode drew electrons from the vapour source to increase ionization. It is, however, also likely that the anode made the whole of the (grounded) chamber and substrates cathodic in the resultant discharge, thereby creating significant secondary electron emission and enhancing ionization. Kobayashi and Doi [8] utilized substrate biasing in addition to the ARE process, and this was sometimes known as Biased Activated Reactive Evaporation. Others utilized a thermionic emitter (in the form of a heated filament) as the electron source [9, 10], thereby avoiding the need for the vapour source to be operating in order to enhance ionization. Another variant was to utilize a filament not only as an electron source to enhance ionization but also to evaporate the vapour [11]. A further approach was to use a hollow cathode electron beam gun vapour source [12, 13], which could also enhance ionization. Figure 2 shows a commercial machine for coating tools with titanium nitride by reactive sputter deposition.
2.2 The Importance of Increased Ionization

There are several reasons why increased levels of ionization are beneficial in PAPVD. In order to appreciate this, it is helpful to understand some basic features of glow discharge plasmas.

The first thing to know is that in a biased substrate system, most of the voltage drop occurs near to the substrate. The "cathode fall" distance is very small, (of the order of millimetres or less), and can be estimated by the Child Langmuir equation [14]:

$$L = \left( \frac{2e}{mJ} \right)^{1/2} \frac{q}{V}$$

Where $\varepsilon_0$ is the permittivity of free space, $J$ is the ion current density, $q$ is the ion charge, $m_i$ is the ion mass and $V$ is the potential drop across the sheath.

The above shows the "free-fall" version of the Child Langmuir equation, and it is important to note that as the cathode current density $J$ increases, the sheath thickness will reduce. A small sheath thickness is advantageous for several reasons: (i) it ensures more uniform ion bombardment around components being coated [15]. This has benefits for phase, structural and temperature uniformity. (ii) It limits the extent of charge exchange collisions in the sheath, which ensures that more ions have energies nearer to the maximum [16, 17].

The energy spectrum for ions arriving at the substrate can be assessed using a model developed by Davis and Vanderslice [18] and modified by Rickards [19]. This reveals that the ratio between the cathode sheath thickness ($L$) and the mean free path for charge exchange ($\lambda$) is critical in determining the energy spectrum of the ions arriving at the substrate [16, 17]. Although there is surprisingly little published information on $L/\lambda$ values, what is very clear is that an increase in the number of ions (and therefore the ion current density) not only increases the extent of beneficial bombardment but also reduces the sheath thickness, thus ensuring that more of the arriving ions have energies near to that achieved by accelerating them through the full bias voltage.

2.3 The Ionization Efficiency

Given the facts above it is clear that any PAPVD system which increases the percentage of atoms arriving at the substrate, which are ionized will provide considerable advantages. This can be evaluated in several ways, but the author has chosen to define the ratio of the number of ions arriving at the substrate ($N_i$) as a percentage of the total atoms arriving ($N_{np}$) as the "Ionization Efficiency". Others have used a measure based on the number of metal (coating) ions compared to the total metal atoms arriving.

The intent of both measures is the same, but the author’s approach has the advantage that it takes account of all arriving atoms (including the background gas), since it can be assumed that the energy dissipation at the substrate surface should take account of all arriving species. For example, at a chamber pressure of 1Pa the number of bombards per cm$^2$ per second is about 2.9 x 10$^{18}$ whereas a titanium film (for example) growing at 1 μm/min represents an arrival rate of about 0.1 x 10$^{18}$ atoms per cm$^2$ per second. Calculating the $N_i$ term is very straightforward, since 1mA/cm$^2$ is equal to a charge flow of 6.24 x 10$^{15}$ ions per second. The Ionization Efficiency $I_{ef}$ is given by:

$$I_{ef} = \frac{N_i \times 100}{N_{np}} \%$$

It becomes clear that at any given current density the calculated ionization efficiency rises rapidly at lower chamber pressures. This leads to a logical question. What level of ionization efficiency is needed in PAPVD? The question should perhaps best be put as “What level of ion current density is needed?” Consideration of data available in the early 1990’s suggested that ion current densities of greater than 4mA/cm$^2$ are needed, and this typically equates to an ionization efficiency of about 4% (depending on the chamber pressure). Such conditions provide coatings with excellent properties. Very interestingly, this level of ionization efficiency can be obtained with all modern PVD systems, whether thermionically enhanced electron beam PVD, arc deposition or unbalanced magnetron sputter deposition [16, 20, 21], (as the main examples).

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A further point to mention is that the above discussion is based on a current density and ionization efficiency model which makes no distinction between metal or gas. In other words, it uses the chamber pressure to define the bombardment, rather than the arriving depositing species. Regardless of the model it has to be said that all investigations of PAPVD have shown that it is important to achieve a high amount of metal ionization. Research by the author and colleagues has indicated that, because of the Penning Ionization mechanism (whereby a gas (eg argon) metastable can ionize a metal atom) it is likely that a high proportion (more than 80%) of the ion current in enhanced plasma assisted PVD systems will be transported by metal (depositing) species. This is a consequence of the lower ionization potentials of metal species compared to gas species. (The single, double and triple ionization potentials for titanium are 15.76, 27.63 and 40.74 eV, whereas the potentials for argon (for example) are 26.83, 13.58 and 27.49 eV (approx.)).

### 2.4 The Bias Voltage

During the first wave of PAPVD, the negative substrate bias levels applied were typically in the kV range. With time, the applied negative voltage reduced to the 50-100 V range and excellent film properties were achieved. This is not surprising, when the energy requirements for different surface effects are considered [17, 18]. Impact ionization typically requires the electron to have an energy greater than 15 eV (depending on the material) and the maximum collision cross section for electron impact ionization is typically 70-100 eV. Sputtering threshold energies are in the region of 15-35 eV. These are probably the main energy-related mechanisms, but one can also cite atom displacement (thresholds 20-50 eV) and gas entrainment (above 100 eV). The energies needed for adatom mobility and for desorption of contaminants is likely to be several eV. So it is not surprising that the second wave of PAPVD saw negative substrate bias levels optimised at 50-100 V.

### 3. The Third Wave

Above, some of the process evolution trends were discussed, along with the improvements in process understanding, which drove those innovations. These were almost all related to increasing the degree of ionization occurring and to ensuring that the deposition volume size was optimized. It was noted, for example, that the arc evaporation process (which derived much of its benefit from the copious generation and emission of electrons from the arc spots) had a wider process window than many other systems. This was attributed in part to the fact that the source of ionization enhancement was located at the vapour source itself. One benefit of this is that the fall-off in depositing flux aligned with the fall-off in ionization-enhancing electrons. It was felt that this would tend to equalize the ratio of the ion bombardment and depositing metal fluxes throughout the chamber. Whether this argument was valid or not, certainly there was a tendency either to locate the ionization-enhancing electron source near to the vapour source (for example in thermionically-enhanced PAPVD) or to trap and confine the electrons to ensure that their effect was maximized throughout the deposition volume (as in the closed-field unbalanced magnetron layout [22-25]).

It should perhaps be mentioned that what seems so obvious to us now (such as the need to close the magnetic field in double cathode sputtering) was not immediately evident to practitioners at the time [26, 27] and anodic enhancement was used widely as an alternative means to trap (and gain maximum benefit from) available electrons [28-30]. Credit should also be given to those who first identified the benefits of the unbalanced magnetron [31, 32] and those who saw the advantages of confining the plasma [33, 34]. These were all the pioneers of the “third wave”, since there seems to be no doubt that the most intensive development activity in PAPVD is now in the sputter deposition field. In particular pulsed power sputtering is providing the means to deposit coatings which were previously difficult to produce. Power supply developments now allow medium frequency AC and pulsed DC power to be applied, for example in the reactive sputtering of oxide coatings.

Figure 3 shows dual rotatable magnetrons in the EOSS optical precision coater [44].

Of course the “third wave” of PAPVD won’t only be the domain of sputter deposition. Arc evaporation continues to take a significant proportion of the commercial PAPVD coating market, especially for tool coating, and a key factor there has been the ability of the process to deposit new multi-component (often nanocomposite) coatings to meet specific application needs. Electron beam PVD is still maintaining its own niche. Especially, the capability of thermionically assisted EBPVD systems (which can enhance the plasma independent of the vapour source) are finding significant benefits for the production of “duplex” surfaces, combining a plasma diffusion treatment with a nanocomposite coating with optimized hardness and elastic modulus properties [45-48].

### 4. Final Comments

These are exciting times for plasma assisted PVD technologies. In this paper three phases of development have been identified. We should not think, however, that the processes of the First and Second wave should be abandoned. There is still a need (for example) for the resistively evaporated aluminum coatings, which came in the first wave. Likewise the processes of the second wave still have a strong presence in the market. Indeed it is interesting to note that Berghaus patented plasma (or ion)
nitriding in the late 1930s and that process is now being combined with PAPVD in advanced “Third wave” processes, which demonstrates that we can always learn from the early pioneers. Those pioneers lacked the technologies which we now have at our disposal, including advanced vacuum pumps, monitoring and control hardware and sophisticated power supplies. Still they made considerable progress towards process developments, which we now treat as routine. What will the “fourth wave” bring? It will surely take advantage of these hardware and software developments. In order to make real progress though, we can expect to tackle difficult process challenges. We shall have to learn to look where we may find it most difficult when we investigate new research ideas. This is known as avoiding the “streetlight effect” – in other words, we shouldn’t necessarily look where it is most easy when we plan and conduct research. Often the main gains are achieved by taking on the biggest (and most risky) challenges.

References
47. A. Leyland and A. Matthews, Optimisation of nanostructured tribological coating, Chapter 12 in Hard Nanostructured Coatings, J. T. M. de Hosson and A. Cavaleiro (Eds.), Springer 2006.

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