The importance of ions in low pressure PECVD plasmas

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Plasma enhanced chemical vapor deposition (PECVD) can be used to fabricate surfaces with a wide range of physical and chemical properties and are used in a variety of applications. Despite this, the mechanisms by which PECVD films grow are not well understood. Moreover, the species which contribute to film growth can be considered quite differently depending on the process. Particularly for functionalized plasma polymer films, the growth mechanisms are considered with respect to the chemistry of the depositing species, ignoring the physics of plasmas. Here we analyse the role ions play in the deposition of three common classes of depositing plasmas, and how these closely related fields treat ions very differently.

Keywords: PECVD, ions, silanes, diamond-like carbon, plasma polymers

INTRODUCTION

While glow discharges were observed as early as 1796 [1] the term "*plasma*" was first coined by Irving Langmuir in 1928 [2]. Plasma discharges of reactive vapors were first reported as early as the 1930 [3], but research interest in plasma deposition started in the 1960s when the physical [4, 5] and chemical [6] properties of some organic plasma deposits were described. Modern plasma deposition techniques include magnetron sputtering [7], ion plating [8], pulsed laser deposition [9], and various plasma enhanced chemical vapor deposition (PECVD) techniques.

PECVD has found use in a wide variety of applications. For example silane plasmas are used in solar cells [10] and microelectronics [11], diamond-like carbon (DLC) coatings are used as hard, wear-resistant barriers for mechanical parts and biomedical implants [12], while soft functionalized plasma polymers may be used to attach biomolecules to surfaces for improved biocompatibility or drug delivery [13]. Recently, plasma deposition has enabled the convergence of technologies in the nano and micro scale range, including controlling interfacial bonding in composites [14], fabrication of nano-thin films for electronic applications [15, 16] and microscale features to control protein adsorption [17].

An important consideration in the growth of all of these types of coatings from plasma is the mechanisms by which film growth occurs (**Figure 1**). As plasma consists of a complex mixture of species with different masses, charges, chemical reactivities and kinetic energies, identifying the species which provide mass to the film can be difficult. However, as discussed later, these species can confer very different properties to the film due largely to the

energy they provide to the surface. Therefore, an understanding of the growth mechanisms is crucial to tailoring film properties. One of the key plasma components are positively charged ions. This is because the electrical fields established by plasmas adjacent to surfaces provide ions with sufficient kinetic energy to promote chemical reactions, and therefore the ions are the engines which drive film growth (either directly or indirectly). The role that ions play though is understood in quite different ways depending on which field of PECVD is being discussed.

DIAMOND-LIKE CARBON FILMS

DLC films were first grown in 1971 [18] and are grown from plasmas of molecules such as methane, acetylene, or larger hydrocarbons. It has been known in this field for some time that the mechanical properties of the film are determined by the energy of the ions arriving at the surface [19]. Additionally, DLC films were originally grown from ion-beam deposition [20]. Therefore, ions have been considered to be important species in contributing mass to the film, and this led to early researchers in the field considering ions almost exclusively. More recently, the role of neutrals has been demonstrated. For example, both Richter et al. [21] and Moller [22] assumed a sticking probability of 1 for ions (probably an overestimate) and calculated for a range of precursors that ions contributed between 25 and 100% to the mass of the deposit, critically depending on the chemical structure of the precursor. As pointed out by Richter et al. [21] "*despite the fact that most authors confine themselves to the ions, in principle both ionized species and neutral molecules must be taken into account as film-forming particles.*" Therefore, in the field of DLC films, ions and neutral species

(intact precursor molecules and radicals) have been thought to be important mass-contributing species.

SILANE FILMS

Reports of films grown from SiH_4 and related compounds and gas mixtures started appearing in the late 1960s [23]. The dominant species are often SiH_x^+, but also SiH_x radicals. From early in the development of silane based films, both neutrals and ions were considered important [24, 25]. Researchers in this field have studied the plasma phase mass spectra of both neutrals and ions [26] and controlled the ion energy to elucidate the role of SiH_x radicals, SiH_x^+ ions and even H^+ ions in the deposition process [27]. A strong dependence on the plasma pressure is observed with Perrin [28] demonstrating that the contribution of ions to the deposit varies between nearly 100% at 0.1 Pa down to around 1% at 100 Pa.

PLASMA POLYMER FILMS

A number of fundamental papers on plasma polymer deposition were published in the late 1960s and early 1970s, including a number of studies looking at the mechanisms of deposition from plasma, including the roles of both ions [29, 30] and radicals [31]. Then in 1979, Shen and Bell [32] correctly showed that in weakly ionized plasmas the ratio of radicals to ions in the plasma phase is of the order of 10^3–10^5. They followed this with a discussion on the role of radicals in mechanisms of deposition, ignoring any possible contribution from ions presumably because they believed the density of ions was so low that any mass deposited by ions would be insignificant. Then in *Plasma Polymerization* Yasuda [33] proposed the rapid step-growth polymerization mechanism (RSGP), which became the most cited work in the field. While Yasuda acknowledged that RSGP could proceed via any "*chain-carrying species*" (including radicals, ions and excited species), all the mechanisms subsequently discussed involved radicals exclusively. Thus, it was implied that ions provided energy to the surface through energetic collisions which enabled further reactions to occur [34], but their role in contributing mass to films was discounted. As discussed below, there is now growing experimental evidence to support ions playing a greater role in plasma polymer growth [35–37].

PLASMA PHYSICS OF IONS

Thus, it can be seen that these related fields approach the issue of ions in plasmas in quite different ways, and accordingly ascribe different importance to ions. In some cases this appears to be driven by historical development of the field. What has been overlooked in some of these studies is some basic physics of non-thermal plasmas. Tonks and Langmuir described the plasma phase as a region of space where the "*densities of ions and electrons are high but substantially equal*" [38]. This is the case in the bulk of non-thermal plasmas and the flux, J, of both neutrals and ions are governed by thermal motion.

$$J = 0.25n\sqrt{\frac{8kT}{\pi m}}$$

where n is the particle density, k is Boltzmann's constant, T is the absolute temperature and m is the particle mass.
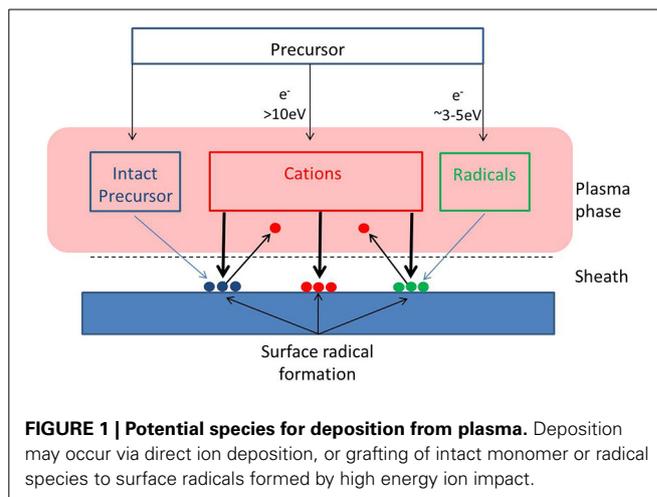

FIGURE 1 | Potential species for deposition from plasma. Deposition may occur via direct ion deposition, or grafting of intact monomer or radical species to surface radicals formed by high energy ion impact.

However, as early as 1949 David Bohm [39] described the effect of placing a surface in contact with a plasma phase. As electrons are lighter and hotter than positively charged ions, the flux of electrons to surfaces is initially much greater than that of the ions. This results in the surface gaining a negative potential relative to the plasma. The surface potential then develops until at equilibrium the flux of positive and negative charged species is equal. Bohm showed that the presence of the surface in the plasma results in the formation of a sheath region adjacent to the surface where the density of charged particles decreases. In fact, there are two distinct regions; the sheath, where the density of the positive ions is higher than that of electrons, and a pre-sheath, where the densities are the same but decrease slightly compared to the bulk plasma. In this pre-sheath region, ions are accelerated such that they enter the sheath at the Bohm velocity, u_b

$$u_b = \sqrt{\frac{kT_e}{m}}$$

where T_e is the electron temperature. The flux of ions, J_i, is then given by:

$$J_i = exp\left(-\frac{1}{2}\right)n_i\sqrt{\frac{kT_e}{m}}$$

where n_i is the ion density in the plasma phase and the $exp\,(-1/2)$ term describes the decrease in ion density in the pre-sheath.

Therefore, the surface has the effect of increasing the flux of positive ions through the pre-sheath/sheath regions to the surface. The increase in flux above the normal thermal flux, J_t, can be mathematically described by:

$$\frac{J_i}{J_t} = \sqrt{2\pi}exp\left(-\frac{1}{2}\right)\sqrt{\frac{T_e}{T_i}}$$

where T_i is the temperature of the ions in the plasma phase, usually close to ambient temperature. Therefore, for a typical electron temperature of ~3eV, the flux of ions is increased by a factor

of $\sim$15 [40]. It should be noted that for DC plasmas, this factor can be even higher [41]. Neutral species, such as radicals and intact precursor, are not accelerated to the surface due to the generation of potentials in the plasma, and so while the density ratio of radicals-to-ions may be of the order of 10^4, the flux ratio, the important ratio for film growth, is substantially lower.

While this phenomenon is well known to plasma physicists, it is often overlooked in the field of depositing plasmas as it is assumed that depositing plasmas are governed by chemical processes [1]. Additionally, one of the assumptions in Bohm's calculations was that the sheath region is non-collisional; in some cases, particularly for silanes and plasma polymers where the pressure can be relatively high, this may not be the case which can affect the ion energy and structure [42].

EXPERIMENTAL EVIDENCE

While the increase in ion flux due to the electric fields generated decreases the neutral: ion flux ratio to around 10^2–10^3, it cannot alone explain how ions can contribute significant mass to the deposit compared to neutrals. Recent experimental evidence shows that ions can be larger than neutrals due to reactions in the plasma phase, and that ions are much more likely to stick to the surface upon impact.

PLASMA PHASE MASS SPECTROMETRY

Analysis of the plasma phase has shown that ions can form large oligomers in the plasma phase. O'Toole et al. [43] demonstrated for organic precursors that ions form large molecules of the form $(nM+H)^+$, where M is the precursor and n is an integer up to 3. This was shown for acids [43], alcohols [44] and amine-containing organics [45]. Simultaneously, the neutral mass spectra were measured by electron impact and dimers were only observed for methyl isobutyrate. It has similarly been measured that silane plasmas exhibit $Si_2H_x^+$ and $SiCH_x^+$ ions when combined with methane [24]. Thus, ion-molecule reactions in the plasma phase have been confirmed.

There is also experimental evidence of a correlation between the ionic plasma species observed and the chemistry of the deposit. Hexamethyldisiloxane plasmas exhibit ion precursor, dimer and trimer peaks; the same peaks are observed when measuring the surface chemistry by ToF-SIMS. The co-ordination of silicon and oxygen measured by XPS also correlates well with the ionic plasma species observed [37].

The mechanism by which large ions grow has been modeled by selected ion flow tube mass spectrometry, whereby a positively charged precursor ion, for example $(M+H)^+$, is reacted with neutral M in a buffer gas and the products measured by mass spectrometry [46]. Reaction conditions were kept close to those in plasma (pressure, temperature) and the resultant product ions at $\sim$2 M, 3 M correlate with those directly seen in plasma. This has allowed some insight into the kinetics of plasma-phase ion-molecule reactions.

STICKING PROBABILITY

It is often assumed, particularly in DLC plasmas, that the sticking probability of ions is 1. However, comparison with calculations for hyperthermal ions [35] shows that this assumed sticking probability is probably an overestimation. This study showed a more realistic sticking probability of between 20 and 50%, and is dependent on the ion energy [37]. It should be noted that this is almost certainly a net sticking probability as ions with energies greater than $\sim$15 eV can simultaneously sputter the growing film [47].

As ions usually have energy greater than 10eV when they arrive at the surface, they can provide enough kinetic energy to promote bond breakage and rearrangement [47]. Neutral species on the other hand rely on chemical energy to attach to the surface. In the case of plasma radicals, this requires that the radical arrive at the surface in the vicinity of an existing surface radical. It has been shown by von Keudell et al. [48] that the sticking probability of methyl radicals is extremely low at $\sim$3 $\times$ 10^{-5}, but this increases to $\sim$ 3 $\times$ 10^{-3} in the presence of atomic hydrogen. They also showed that even a plasma radical colliding with a surface radical only results in a sticking probability of $\sim$50%. This probability may be even lower for larger radical species as steric and collision orientation effects become important [49].

Combined, these analyses show that while the density of neutrals and radicals in the plasma phase may be extremely high relative to ions, the combination of increased flux due to sheath formation, plasma phase oligomerisation and higher ionic sticking probability demonstrates that both ions and neutrals should be considered as contributing mass to plasma deposits.

IMPLICATIONS
DEPOSITION KINETICS

The role that ions plays in depositing plasmas compared to neutral species has a profound effect on the kinetics of deposition [43]. It has been shown that the deposition of saturated precursors is dominated by ionic processes while precursors which contain sites of unsaturation can deposit via neutral grafting [50]. There is a strong negative correlation between the degree of neutral grafting and fragmentation of the precursor in the plasma phase; thus for unsaturated precursors, neutral grafting dominates the kinetics at low plasma power and high pressure, but ionic processes increase in importance when the power is increased or the pressure decreased. Similar results have been shown for DLC films for methane and acetylene plasmas [51].

The contribution of ions to the deposition process also opens the possibility to control the kinetics using measureable plasma parameters, such as ion flux. This was first demonstrated in 1971 when the DC bias on the substrate was varied between +60 and −350 V [29]. Applying a positive bias decreases the positive ion flux and ion energy and Westwood showed that at high enough bias, the deposition stopped (note that intact precursor and radical species could still diffuse to the substrate but no deposition was observed). Decreasing the bias resulted in a linear increase in deposition rate until–100 V when the deposition rate decreased again, presumably due to ion etching becoming important. Similarly, the flux of ions to substrates can be used as a process parameter to transfer plasma processes between reactors [52].

FILM PHYSICAL AND MECHANICAL PROPERTIES

It has been well known in the field of DLC plasmas that ions play the dominant role in determining the mechanical properties

of films. Pappas and Hopwood [53] and Peter et al. [51] measured an increase in the film hardness for methane plasmas up to bias voltages of ∼200–300 V, followed by a slight decrease at higher biases. For methane the trend was largely independent of pressure, however for acetylene the hardness decreased with increasing pressure. These results correlated with the contribution of ions to the deposit (methane ∼60%, acetylene ∼20%) and the ion energy flux to the film per deposited carbon atom. For silane plasmas, the role of ion energy in determining the crystallinity of the film has also been shown [27].

In the case of functional plasma polymers, the trends are less clearly defined. Hegemann et al. [54] for example showed that increasing the momentum flux density (dominated by ion contribution) resulted in densification of NH_3/C_2H_4 copolymer films. Similarly, increasing the ratio of NH_3 : C_2H_4, and therefore decreasing the amount of unsaturated precursor in the plasma, resulted in denser films [55]. Conversely for lower energy density film formation, saturated precursors result in less dense films but with increased elastic modulus [56] due to high cross-linking. Typical ion energies for plasma polymer deposition are 10–50 eV, while for DLC plasma deposition the ion energy can be an order of magnitude higher. Even higher ion energies (∼20 keV) can be utilized in plasma immersion ion implantation [57] which effect long lasting chemical changes to a depth of around 30 nm. These studies highlight the key role ion energy plays in depositing plasmas.

CONCLUDING REMARKS
While the fields of DLC, silane and plasma polymer surface coatings share some similarities, the way they have approached the role of ions in deposition is quite different. In recent years there has been a slight convergence of ideas, with recognition by plasma polymer researchers that many plasma species, including ions, may contribute mass to surface coatings from plasma. The role that ions play is unique in that they not only can provide mass, but also dramatically affect the chemical and physical properties of the film due to their high energy. Further understanding of the role of ions in this regard will help develop better films and control of plasma polymer processes in the future.

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