Process Benefits of Wide Area, Low Energy End-Hall Ion Source for Surface Pre-Cleaning and Functional Treatment of Polymeric Substrate Materials

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ABSTRACT

The low ion energy and high current flux of broad-area gridless end-Hall ion sources can have significant advantages over high-energy gridded or gridless ion source systems when processing glass and engineering thermal plastics. Specifically, the lower energy spectrum of such ion sources are shown to improve surface energy and adhesion with limited process exposure times and while inducing very limited optical, thermal or sub-surface layer damage which leads to mechanical embrittling, deformation and optical yellowing. We examine fundamental surface treatment properties of multiple materials (glass, polyamide 6.6, polycarbonate, thermoplastic polyurethane, poly(tetrafluoroethylene), and polyethylene terephthalate) when processed under identical conditions in pure oxygen and argon-oxygen blends using contemporary end-Hall ion source technology. Water contact angles, optical transparency, substrate thermal damage of treated surfaces are reported along with adhesion performance of PVD sputtered titanium and diamond-like carbon films. Optimal reduction in surface contact angle is noted for most all materials with the inclusion of 15-30% of oxygen with little to no change in optical transparency. In addition to these results, typical treatment rates are deduced against ion beam current dosage to help process developers scale end-Hall ion source systems to various wide-area batch and in-line vacuum treatment applications.

INTRODUCTION

Deposition of metal coatings on polymers requires surface activation (etching) in plasma to achieve high adhesion. In principle, plasma treatments remove weak surface layers on the polymer by oxidation, clean by removal of adsorbed materials, crosslink the sub-surface region and lead to the introduction of chemical functionalization by reactive chemical species (oxygen, fluoro carbons, etc.) [1].

For over 20 years, gridless end-Hall ion sources have been widely used for in situ cleaning and ion assisted deposition in many thin-film processes. These ion sources utilize a magnetically supported plasma space-charge in front of a conical anode to trap and circulate energetic electrons and to generate and accelerate a broad spatial distribution of ions over wide process areas. [2,3] End-Hall ion sources provide high ion current flux densities (1-10 mA/cm²) at low ion energies (~100 eV and less), typically with a broad ion energy distribution. In pre-clean or surface modification applications, the high flux and broad ion energy spread of end-Hall sources enables useful etch rates while limiting or avoiding substrate damage that might otherwise occur with the relatively higher mean ion energy (0.3 – 2 keV) observed with high-energy gridded ion sources or gridless anode layer ion sources [4].

Since their introduction, end-Hall sources have been most widely used for treatment of glass and polymer substrates in optical, ophthalmic and tribological coating industry. In conventional industrial practice, pure Ar is used for pre-clean or pre-treatment to aid in polymer surface modification and subsequent film adhesion, while reactive gases (oxygen, nitrogen, etc.) are generally reserved for ion beam assisted densification and stoichiometric control of optical or tribological films [5]. When using the end-Hall source in a conventional surface pre-treatment step, workers have noted that the use of pure Ar results in sputtering of non-anode ion source components. This will often limit the mean-time-between-maintenance (MTBM) of the source assembly. However, it is known that component lifetimes are extended by at least ten fold when even small percentages of O₂ are added to pure Ar process steps. This has very important ramifications to process engineers hoping to scale end-Hall technology to numerous high-rate, wide-area industrial vacuum coating applications, where MTBM may need to be on the order of hundreds of hours. To date, detailed material surface science of Ar-O₂ plasma or ion beam exposure of polymers has been very limited. Thus the aim of the current study is to fully examine and optimize polymer surface pre-treatment features and film adhesion by means of Ar-O₂ ion beam exposure from contemporary end-Hall source technology.

EXPERIMENT

Materials, activation and coating

For this study we used 1mm thick technical-grade polymer sheets, including polycarbonate (PC), polyamide (PA) 6.6, poly(tetrafluoroethylene) (PTFE), polyethylene terephthalate (PET), thermoplastic polyurethane (TPU), and float glass substrates, which were cleaned with ethanol (99.5%) and dried before mounting in the process vacuum chamber. The applied industrial-like batch coating system (Figure 1, [6]) allows one to coat substrate parts up to 530 mm diameter and
400 mm height at different service positions by means of DC (pulsed) magnetron sputtering and plasma pre-treatment with an end-Hall ion source. After pumping down the chamber to 2x10⁻³ Pa base pressure, the pre-treatment was performed with a high-power, water-cooled Veeco end-Hall ion source with hollow-cathode electron-source and Veeco Mark III+ Source Controller. The source-to-substrate distance, D, was 130 mm and initial sample temperature was 30°C. Rotation of the substrate barrel was applied to simulate batch coating.

After finding optimal pre-treatment parameter settings, magnetron sputtering was used to subsequently deposit thin diamond-like carbon (DLC) and titanium coatings both on the plasma-treated polymer surfaces with no venting of the chamber as well as on untreated, virgin polymers. For DLC deposition we used pulsed DC sputtering (80 kHz, 1 µs pulsing parameters) at 2 kW power at the electro-graphite target in pure argon atmosphere, for Ti deposition DC sputtering at 1 kW power from a grade-2 Ti target.

Materials Characterization
Film characterization of polymer and glass materials was focused onto the application oriented parameters of the pre-treatment and film deposition. At ~10-15 min. immediately after the End-Hall plasma treatment, we performed contact angle measurements on a custom test assembly with de-ionized water droplets (1 µl size, 20°C, 50% relative humidity). Light transmission measurements were performed with an OceanOptics HR4000 optical spectrometer and white light source with exemplary data reported for wavelengths averaged between 596 and 604 nm. Adhesion was tested with an adhesive tape pull-test followed with light microscopy to detect micro defects such as film delamination or micro-cracking.

Thermal Probe and Ion Beam Current Density
Thermal probe and ion beam current flux measurements were made to deduce the incident power flux to the thermally sensitive polymers. The temperature probes comprised a thermocouple placed 0.5 mm beneath the surface of a polyamide 6.6 cylinder held statically in front of the ion source. Ion beam current density measurements were surveyed by conventional Faraday cup probe (-30V bias) on the same model end-Hall ion source in a separate vacuum chamber (yet operated at conditions nearly identical to those observed in the process vacuum chamber). The thermal probe and Faraday cup measurements allow us to characterize the results in terms of incident ion beam power and ion current flux and dosage, rather than rely upon user input variables that are specific to the ion source model or process chamber scale. Incident ion beam metrics can be more helpful to interpret and scale the process results.

RESULTS
End-Hall ion source operation is typically characterized by DC anode voltage ($V_A$), DC anode current ($I_A$) and total input gas flow. For typical end-Hall source operation, the anode voltage is fixed and the current (or DC discharge impedance) is regulated by minor adjustments to the total input gas flow. The end-Hall anode voltage typically determines the ion energy spectrum (or mean beam energy) and the anode current generally determines the ion current flux density (mA/cm²). End-Hall source input gas composition can also strongly influence ion current flux, but also determines effective ion mass, vacuum pressure and concentration of chemically active species. In these results, we examine the influences of source operation (mean ion energy and ion flux), gas flow composition (Ar:O₂) and net beam exposure times on the chemical and physical surface properties of treated polymers and glass.

Figure 2 shows the typical change in contact angle of the treated samples with discharge of 110V and O₂ flow at 30% over Ar. In this instance, the on-axis beam current flux, J, was ~1.1 mA/cm². All investigated plasma treatments resulted in decreased contact angles (Figure 1a) with increasing “plasma exposure time”, which conservative estimate of rotated substrate ion beam exposure against a +/-20° angle with respect to the source axis. The contact angle of the investigated hydrocarbon polymers reached a plateau of < 20° after 40s. of plasma exposure, while for glass < 20s. of plasma exposure is sufficient for full wettability, (contact angle < 10°). Plasma exposure of PTFE resulted in decreased contact angles (from 115° to ~90°).
As expected, the wetting behavior is highly influenced by the O₂ content in the gas mixture as shown in Figure 3. For 40 s plasma exposure, 15 vol.% O₂ is sufficient for contact angles < 10° for PA 6.6 and glass, while the other polymers require 30 vol.% O₂ for such wetting performance. By contrast, wetting of PTFE is only weakly influenced. Peak ion beam current density (1.0-1.2 mA/cm²) and integrated ion beam dosage were similar for pure Ar and Ar:O₂ blends between 10 and 30%, but was substantially higher (1.8 mA/cm²) for pure O₂ for identical ion source V_A and I_i settings. Only TPU shows a statistically significant increase of its contact angle for pure O₂ when compared to all other Ar:O₂ blends. In contrast, different anode voltages influence surface wetting only slightly as shown in Figure 4 over the range tested. We should note that the anode current setting for data in Figure 4 was 25% lower than for Figures 2 and 3 resulting in a proportionally lower peak ion beam flux (0.8-0.9 mA/cm²) and total ion beam dosage. This lower ion beam dosage may account for slightly elevated wetting contact angles seen in Figure 4 for select test materials at V_A = 110 V.

The effect of the anode voltage on the light transmission is shown for transparent glass, PC, and PET samples in Figure 5 test conditions similar to Figure 4. While treated glass shows a very slight increase, the transmission for the treated polymers is slightly, but not significantly decreased. [Note: A similar trend was seen for the entire optical transmission spectrum between 500 and 800 nm.] Over the range of anode voltage tested, these results indicate low or negligible surface metal contamination and polymer substrate damage when using Ar:O₂ blends through the end-Hall source. [Comparative transmission test for pure Ar pre-treatment were not made in this study.]

As mentioned earlier a static thermal probe was used to examine relative trends in the power flux load to the substrates. Specifically, by observing the initial linear temperature rise of the probe within the first 20-100 s of source operation, we could quantify the intrinsic ion beam power flux separate from the influence of source, substrate or fixture radiant heating. In this system, our best estimates of ion beam power flux were between 30 and 60 mW/cm². The power flux was clearly influenced by total input power variables to the
source \((V_A \cdot I_A)\) and was only weakly dependent upon the Ar:O\(_2\) ratio. Higher pressure operation, typically induced by low \(V_A\) settings with high gas flows, would result in lower power flux readings. Also, we noted that 100% O\(_2\) operation would provide significantly lower power flux density despite its much higher beam current values. This can be explained in part by the lower effective ion mass of O\(^+\) and Veeco’s observation of lower mean ion energy in end-Hall sources when compared to pure Ar and Ar:O\(_2\) operation.

Post treatment adhesion of 900 nm thick titanium and 300 nm thick DLC coatings is shown in Figure 6. for select polymers and glass against various O\(_2\) concentrations for fixed end-Hall \(V_A\) and \(I_A\) settings and exposure times. Adhesion of titanium coatings (Figure 6a) is equally improved for Ar and Ar:O\(_2\) beam exposure for PC, PA and glass, but only improves for PTFE with 30% to 100% O\(_2\) content. DLC coating adhesion (Figure 6b) is typically adequate for hydrocarbon surfaces (PC and PA) and is not negatively impacted with the surface pre-treatment irrespective of O\(_2\) content. DLC adhesion to glass is improved by the Ar:O\(_2\) pretreatment. Conversely DLC adheres poorly or at least inconsistently to PTFE but is improved (without process optimization) with pure O\(_2\) ion beam exposure.

**Figure 6:** Adhesion tape pull-test results for (a) Ti and (b) DLC coatings over PTFE, PC, PA and glass under various O\(_2\) concentrations. [Refer to Figure 3 for details on process conditions and settings.]

**DISCUSSION**

In end-Hall source operation, ions are generated in the discharge plasma and accelerated into the ion beam. However, the surface is exposed to various excited species and forms of energy besides to the incident energy of the ions (with mean kinetic energy, which is typically ~50% of the anode potential). Other forms of energy principally include ion/electron recombination energy (10-30 eV), thermal radiation from the source and process chamber boundaries, and photon radiation from the source discharge (UV photons (200-400 eV), vacuum photons (< 200 eV)). All these energies are absorbed by the substrate surface and assimilated to surface modification and thermal heat transferred to the substrate. Cooling of the thin substrates is only possible by radiation to the chamber walls and thermal conduction to the substrate mounting plate [7]. The results of the static thermal probe measurements indicated rather negligible influence of thermal radiation from the end-Hall source and its electron source. The thermal probe measurements also confirmed that the net substrate surface input power was proportional to the product of mean ion energy (anode voltage) and beam current density (anode current). The substrate temperature at some 100 µm below the surface is generally expected to be lower than on its surface due to the poor thermal conductivity of polymers, as quantitatively shown by Trakhtenberg et al. [8]. Nevertheless, no samples in this study were apparently overheated given the short pre-treatment exposure times.

While excessive surface temperatures would result in depolymerized substrate surfaces and ultimately deformed substrates, moderately elevated temperatures increase the surface reactivity for modification. Oxygen species are the primary reactive species for polymers leading to both (1) the oxidation of contaminating organic material at the surface (cleaning effect) and (2) the initialization of modification reactions [9-11]. These modification reaction with ionic, atomic or molecular oxygen lead to the formation of polar functional C=O, OH, and CO\(_2\)H groups on the polymer surface [12,13]. In contrast, UV radiation and the inert gas ions/atoms of noble gas plasmas (e.g., He or Ar) were found to be effective in creating free radicals, but do not add new chemical functionalities from the gas phase [14,15]. However, the functional groups and radicals could remain active for only short time after plasma treatment. (Exposure to other gaseous environments can result in radical quenching.) Advantageously, this surface conditioning effect is used for subsequent film deposition since vaporized metal atoms can covalently bind to the polymer surface.

Although we have only contact angle measurement data, we take for granted that the rise in hydrophilicity is due to the more polar character of the surface, which is supported by many findings in the literature [16-20]. The polar component of the surface free energy arises from the orientation of permanent electric dipoles (e.g., functional groups like C=O, OH, CO\(_2\)H, and H) by dipole-dipole and charge transfer interactions [21,22].

Generally, oxygen plasma treatment leaves many polymers more wettable than inert plasma treatment by increasing the number of functional dipoles, and is demonstrated in our investigations too, when comparing the results obtained for pure argon and pure oxygen (Figure 2). Thus, we should expect that
mixtures of Ar and O₂ (e.g., 30 vol.% O₂) are beneficial for some polymer materials (TPU, PET). Since polymer surface roughnesses (measured but not reported here) were seen to substantially decrease after surface treatment, we conclude that the improved adhesion result is mainly attributed to the modification of the chemical composition and functionalization of the treated surfaces.

Of all the polymers tested, PA was found to be the most receptive to surface functionalization. For most all hydrocarbon polymers, saturation with oxygen containing polar groups on the surface seems to occur even at low O₂ contents (15 vol.%) in the end-Hall plasma, given sufficient exposure time or ion beam dosage. Also for glass, such saturation with oxygen can be an explanation for the low contact angles found in oxygen containing plasma treatment. Aromatic rings (found in PET and PC) are generally non-polar and stabilize the polymer. Thus, for PC and PET more intense ion beam exposure and a greater percentage of O₂ in the ion beam gas mixture is demanded as observed in the trends of Figures 2 and 3.

The degree of enhancement in etching or modification due to ion bombardment generally depends on the dose of ions incident on the surface (that is, the ion density, mean energy, and duration of exposure). Reaching the stable plateau reflects the ion dosage necessary for quite full saturation of the surface with oxygen containing function groups (Figure 2). About 40s. of Ar:O₂ plasma exposure at ~1 mA/cm² supplies enough etching and reactive oxygen for occupying all favorable bond sites to reach high wettability. The lack of any strong dependence on source anode potential (Figure 4) is attributed to the very broad ion energy distribution that is characteristic of end-Hall sources [2,3]. For V_a = 90 to 120V, the distributed “band-width” of ion energy does not vary and thus the integrated effect of energy-specific surface reactions is only weakly influenced by the source’s V_a input settings.

The practical adhesion (bondability) between polymer surfaces and other materials deposited onto them cannot always be correlated with wettability [23,24]. The presence of a highly wettable, but weak, boundary layer leads to a low value of practical adhesion. Such weak boundary layers can result from excessive chain scission processes and/or lack of crosslinking at the surface [25], or surface contamination. However, the results of the adhesion tape tests performed on the end-Hall plasma activated surfaces with sputtered coatings indicates no formation of weak boundary layers. Moreover, significant hardening of the polymer surfaces cannot be expected because of the very low ion penetration depths (< 5 nm).

The adhesion of metals on polymers mostly correlates with the formation of a metal-oxygen-polymer complex at the surface [26]. Metals interact with hydroxyl (-OH), carbonyl (-C=O) and ester (-COOR) groups, while atoms in energetically deposited carbon films can directly bond to carbon atoms in the polymer chains (e.g., by etching H or OH). This behavior is reflected in the tape adhesion tests: DLC films excellently adhere on the untreated and treated PA and PC. For glass and PTFE plasma treatment is required to achieve adhering DLC and Ti films. For Ti sputtering, even PA and PC require plasma pretreatment for surface activation. For PTFE, the adhesion is dependent on the oxygen content, while the achieved contact angles are not significantly varying.

When scaling the treatment process to different system scales, it appears that beam current flux (or dosage) at the appropriate Ar:O₂ gas ratio is the key metric. In this work, the end-Hall source discharge current (and thereby beam current density) was intentionally limited to explore the viability of the Ar:O₂ input gas chemistry, which enables longer ion source MTBM and reduces the likelihood of downstream surface contamination. However, it is fully possible to arrange single or multiple end-Hall sources to supply beam current densities as high as 5 to 10 mA/cm² at relatively short process distances (~10 cm) [3,27] and, thereby, reduce the beam exposure time as might be required in high-throughput batch, web or in-line applications.

CONCLUSION

The current work focused on etching of and sputter-coating on glass and a wide selection of polymers with the goal to achieve high adhesion with Ar:O₂ pre-treatment using an end-Hall source. Surface functionalization was examined by means of water contact angle, optical transmission and adhesion of sputtered carbon and titanium coatings against plasma treatment exposure times, beam energy and current flux and O₂ gas content. Reduction in water contact angles (<10° for PA, PC, glass and <20° for TPU, PET) for > 40s. treatment indicated a high impact on the chemical surface composition (formation of functional groups) by the oxygen-species within the ion beam and little to no evidence of bulk substrate damage. Evidence of surface smoothing and the plateau surface wetting at O₂ ≥ 30 vol.% revealed the saturation of functional groups on the polymer and glass surfaces. The influence of end-Hall mean ion energy (anode voltage) was found to be less pronounced than ion beam current flux density. Finally, the coating adhesion was highly improved by all plasma treatments.

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REFERENCES


