Hollow cathode plasma sources for large area surface treatment

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Abstract

Plasma generation over large areas using a hollow cathode discharge is described in this study. Radio frequency linear hollow cathodes in several arrangements, for operation at reduced gas pressure and suitable for scale-up, are presented. Examples of surface processing and coating by PVD, both by hollow cathode discharge (HCD) and hollow cathode arc (HCA), are given. A non-equilibrium atmospheric plasma source utilizing a fused hollow cathode (FHC) with its modular concept can be used for surface treatment, activation or cleaning of temperature sensitive materials at ambient atmosphere. Results on polyethylene and polyethyleneterephthalate activation are presented. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The hollow cathode exhibits a hollow cathode effect — large increases in current density with reduced separation of the two cathodes. The configuration of the hollow cathode, i.e. two walls at the same potential can be realized by different geometries: by two parallel plates, cylindrical shape or even by a wire shaped into a spiral. The concept of the radio frequency (rf) hollow cathode for activation of gas and for deposition of films was patented in 1985 [1]. The cathode sputtering in the hollow cathode discharge using dc generation was known and published even in the sixties [2]. It was reported in [1] for rf hollow cathodes and confirmed also for dc hollow cathodes [3], that the film deposition rates can be enhanced by maintaining the gas flow through the cathode. However, the processes in the hollow cathode do not need to be limited only to sputtering. The system is very flexible and can work both in PECVD (see e.g. [4]) and PVD regimes as well as in etching regimes [5]. It was experimentally proven that both sputtering and evaporation can contribute to the PVD process, depending on parameters and that at elevated powers the hollow cathode discharge (HCD) can be transferred into the hollow cathode arc (HCA) [6].

The hollow cathode exhibits many advantages: (i) high electron density, high activation degree of species; (ii) the discharge is from its principle non-equilibrium; (iii) geometry enables a high ‘heat transfer efficiency’ from the metastable assisted reaction [7]; (iv) gas activation is very efficient when gas flows through the electrode; (v) HCD can be transferred into HCA; (vi) the system is versatile and scalable; and (vii) PVD and PECVD can be operated simultaneously.

In this work we present novel hollow cathode based plasma sources for large area processing at both reduced and atmospheric pressures.

2. Low pressure radio frequency linear hollow cathode concepts and designs

The first design of a linearly scalable source, the linear arc discharge (LAD) source [8,9] was based on an rf generated hollow cathode discharge between two parallel plates with a confining magnetic field. The confining magnetic field perpendicular to the cathode plates promotes the pendulum motion of hot electrons between the plates and facilitates the hollow cathode effect, simultaneously providing high power density.
The linear hot zones are formed at the plate surfaces due to an ion bombardment inside the hollow cathode. This process depends on the magnetic field configuration. For definite parameters of gas flow rate, generation power, gas pressure, etc., the stationary magnetic field can be optimized to achieve a uniform distribution of the plasma density along the slit. However, any change in the discharge parameters or the gas dynamics during operation of the LAD source are reflected by changes of both the particle velocity components and the distribution of the electric field in the discharge. Then the ions may be deflected towards one side of the hollow cathode slit which may result in a non-uniform release of the cathode material and consequently in a non-uniform processing rate on the substrates.

Recently we have developed a new plasma source, the magnets-in-motion (M–M) rf linear hollow cathode, which is not sensitive to the parameter changes described above. The static magnets are either replaced by or combined with the rotary permanent magnet systems [10,11].

Fig. 1 shows the most simple arrangement, with two permanent magnet systems placed opposite to each other and a driver system for moving the magnet systems. Experimental results show that the discharge characteristics respond to the character of the motion. For instance, the rotary motion of the magnet systems provides a time variable distribution of magnetic flux lines, i.e. time variable distribution of plasma characteristics. This brings about a symmetrization of, e.g. saturation ion current, electron temperature, emission from the plasma and the wall temperature along the slit and is reflected by a uniform distribution of the deposition rate along the cathode slit.

The performance of the source reminds pulsed regime, however, the discharge is never interrupted and even in time periods when the hollow cathode effect is not promoted, the discharge attains extraction abilities. The most important difference is however the sequential character of the discharge development (pulsing) along the slit. In most experiments, 100-mm long cathode plates were used. Now, the M–M LOC 180 source is being tested, with the length of plates 180 mm.

Ongoing development of a new hybrid reactor combining the M–M rf linear hollow cathode with a microwave ECR plasma is an innovative step to a new generation of high density plasma sources [12].

3. Reactive deposition by the M–M rf linear hollow cathode

An extraordinary feature of the reactive process in the hollow cathode acting as a target in the PVD process is the absence of the hysteresis effect. We found this to be valid not only for small cathodes but also for linear cathodes with the target areas and pumping speeds comparable to those used for magnetron sputtering [13]. The deposition rate of the compound is often higher than the deposition rate of the target metal [14,15] and the target condition was observed to play a less important role than the properties of the gas.

The effect of special mixtures of nitrogen with argon for the titanium rf hollow cathode was already presented in several papers, see [14]. At low nitrogen content in argon, the quenching of argon metastables by nitrogen molecules brings about a thermal energy gain, promoting the transition of the process into the hollow cathode arc (HCA) regime. At low nitrogen content in argon and above a certain power the deposition rate of TiN is up to 30 times higher than that of Ti at the same parameters. The TiN is of close to stoichiometric composition and exhibits a microhardness of 2600 HV. The superior properties of TiN films grown in the HCA regime result from the high incorporation of Ti+ and N2+ into the film [14,16].

Fig. 2 illustrates the process of TiN deposition by the M–M rf linear hollow cathode. The ‘metal release’ rate monitored by the optical emission from Ti and Ti+ was examined to see the relation with the deposition rates. When metal release is monitored from inside of the linear hollow cathode against the cathode outlet, the emission intensities (and the temperature at the cathode walls) attain very sharp maxima at 0.016% N2 as a result of the metastable assisted reactive process. When the metal release is monitored outside the hollow cathode, from the plasma channel with the decaying plasma, a shift is observed, caused by changing discharge characteristics after discharge is forced out from the outlet of the cathode. The pressure between the cathode plates is higher than the pressure in the chamber and the particle motion inside the hollow cathode is not affected by the anode (rf plasma itself). The broad maximum of the metal release rate at 0.1% N2 is accompanied by a
maximum in the deposition rate of 2000 nm/min at the same nitrogen content and a broad maximum in the saturated ion current measured by the Langmuir probe 15 cm below the center of the cathode outlet at approximately 0.15% N₂. It is clear that for optimization of the reactive deposition of films, the data from the decaying part of plasma are of utmost importance.

Two photographs in Fig. 3 show the argon M–M rf linear hollow cathode discharge using Ti plates, delivered power being 1200 W and the M–M plates with hot zones after the discharge was turned off.

Replacing nitrogen by oxygen as a reactive gas, the TiO₂ film deposition process was investigated. It is possible, by changing process parameters, to gradually tune the crystallinity of the TiO₂ film from rutile, through rutile–anatase mixture, to anatase structure. It should be noted that films were deposited without heating the substrates. The deposition took place in the hollow cathode discharge (HCD) rather than in the hollow cathode arc (HCA) mode. The higher the contribution of Ti ions the more the phase is shifted to rutile. The grazing incidence XRD diagram from the anatase TiO₂ film deposited on soda-lime glass is in Fig. 4.

The M–M rf linear hollow cathode source was tested also in the low power regimes. The example is deposition of ZnO:Al films where the power limit for given configuration and for low melting point Zn:Al target was 350 W. The film resistivity within the processing window at 0.5% O₂ was 8 × 10⁻⁴ Ω cm. Because of the low power the deposition rate is much lower (100 nm/min) as compared to, e.g. hot cathode arc deposition of TiN (2000 nm/min).

4. Oil removal from Al foils using the M–M source

A broad interval of experimental parameters was examined to find the optimum regime for oil removal from Al surface. The effect of the M–M rf linear hollow cathode plasma treatment was evaluated by the contact angle dynamic measurements (FTA 200). The pendant drop of a precisely defined volume is released after triggering and the shape of the sessile drop is scanned very fast, within fractions of seconds. Fig. 5 gives a comparison of the contact angle time developments in...
the range up to 45 s, for untreated Al foil and Al foils treated 1 and 30 s, respectively, in the oxygen M–M discharge. The values given in the plot are not the final values: during 3 min the sessile drops are flattened further and reach 5.95 and 13.638, respectively. The shape of the drop at the untreated foil surface remains unchanged, though. It is justified to say that the contact angle values measured after several minutes are those given in most reports where manual measurements were used. Fig. 6 summarizes contact angle evaluation as a function of treatment time in the M–M oxygen plasma. The full curve represents the evaluation immediately after the drop is deposited onto the surface, the dashed curve corresponds to the values derived after approximately 3 min.

From the point of view of industrial applications the speed of moving foil below the source is important for the process cost. We can estimate, that the speed of 100 m/min corresponds approximately to the treatment time of 3 s, given by the configuration of the M–M plasma source used. The M–M LOC 180 source with a plate length of 180 mm can be scaled even to longer plate size.

5. Fused hollow cathode (FHC) cold atmospheric plasma source

Increasing the pressure, the dimensions of the hollow cathode must be reduced to retain the hollow cathode effect. We tested successfully a single hollow cathode with the inner diameter of approximately 400 μm operating at atmospheric pressure [17]. For large area applications, two new systems that unify atmospheric rf hollow cathode discharges in the integrated open structure with flowing gas were developed recently [18]. The structure is placed either into a cylindrical electrode cartridge-HEIOS (hollow electrode integrated open structure) or into a rectangular electrode cartridge-HEIOS (hollow electrode linear integrated open structure). The latter one, where the uniform fused hollow cathode (FHC) discharge is excited over the area of 20 cm², is shown schematically in Fig. 7. The scale up into much larger areas is possible. The discharge is homogeneous, luminous, does not exhibit streamers or filamentary structure and fills the volume between the FHC and counter electrodes. The FHC is also very stable, operating hours without any disturbances, it is easy to ignite and power consumption can be as low as several tenths of W/cm² of the electrode active area. In most experiments the discharge was operated in an open chamber, with access to air.

6. Activation of plastics

The low power density allows the use of the fused hollow cathode cold atmospheric plasma source for treatment of plastics. The polyethylene (PE) and polyethylene terephthalate (PET) surface activation was tested using the HELIOS arrangement. The 10×2 cm² plastics strips were placed directly into the Ne+air discharge, on the sample holder. The forward rf power was varied between 7 and 30 W and the exposure time between 1 and 30 s. The surface tension was measured by assessing...
the wetting of inks (DIN 53364). The values of surface tension on PE increased from the value of $\leq 34$ mN/m to values $\geq 56$ mN/m. The PET results exhibited an increase from 36 mN/m to values $\geq 56$ mN/m.

Dynamic contact angle measurements after comparable treatment in the last version of the HELIOS system are shown in Fig. 8. Scanned values of the contact angle on the untreated PE surface and on activated PE surface in the Ne + air plasma clearly demonstrate the effect of the FHC discharge. The stabilized values of 84.5° and 56.5° correspond to 33.5 mN/m and 57.5 mN/m, respectively, similarly as we obtained from the wetting inks assessment with the preceding version of the HELIOS system. Results from FTIR spectroscopy indicate dehydrogenization and formation of C=C bonds which is reflected in an increase of surface energy and of binding ability to metal.

7. Conclusions

The magnets-in-motion (M–M) arrangement was applied in the rf linear hollow cathode system bringing about a qualitatively new type of linear hollow cathode plasma source for large area processing. The character of such a source, with time and space controlled discharge is reminiscent of a special sequentially pulsed plasma. The M–M rf linear hollow cathode can be used for a variety of deposition processes, both in hollow cathode discharge and hollow cathode arc regimes. The M–M source was successfully tested also for oil removal from aluminum foils. The process can be used for large area moving substrates.

The fused hollow cathode cold atmospheric plasma source based on the rf hollow cathode discharges generated simultaneously in the integrated open structure represents a new very efficient source for large area processing. The concept of the FHC makes the source extremely suitable for scale-up and flexible for different large area applications. A uniquely low power consumption enables surface treatment of temperature sensitive materials.

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References

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