Surface & Coatings Technology 322 (2017) 174–201

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Atmospheric pressure non-equilibrium plasma jet technology: general features, specificities and applications in surface processing of materials

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ARTICLE INFO

Article history:
Received 2 February 2017
Revised 9 May 2017
Accepted in revised form 11 May 2017
Available online 12 May 2017

Keywords:
Plasma jet
Atmospheric pressure non-equilibrium plasma
Surface processing
Plasma treatment
Plasma-assisted deposition
Plasma etching

ABSTRACT

Atmospheric pressure non-equilibrium (cold) plasma jet technology received enormous attention in surface processing of materials in the last two decades, and still continues nowadays to attract growing interest. In addition to the advantages of the atmospheric pressure operation such as the potential cost reduction of apparatuses as well as their easier handling and maintenance, due to the distinctive remote operation, plasma jets give the unique possibility of placing the substrate outside the source boundaries. Consequently, the processing of complex three-dimensional objects and the integration into existing production lines are expected to be much easier. However, while appealing, plasma jet technology has the drawback that great efforts are required for process optimization, since many factors can affect, for instance, the physical and chemical proprieties of the so-called "plasma plume" emanating from the devices and propagating in open space towards the substrate to be treated. The aim of this paper is to provide a critical literature review on the utilization of atmospheric pressure non-equilibrium plasma jets in surface processing of materials. Starting from the description and classification of the multitude of devices used in this applicative field so far, the attention will be drawn on some very important aspects to be taken into account in process optimization. The discussion will be focused on basic concepts and peculiarities closely related to the remote operation of the plasma sources, which include the characteristics and dynamics of the plasma plume interacting with the substrate and the surrounding atmosphere. Since the plasma jet approach allows the surface modification of small localized regions of the sample, the strategies implemented to enlarge the treated area will be also addressed. Finally, a brief overview will be given of the available applications and recent developments in the field of etching, thin film deposition and treatment.

1. Introduction

Atmospheric pressure non-equilibrium plasma jet devices (also referred to as non-thermal or low-temperature or cold plasma jets or torches) can be defined as remote plasma sources operating at atmospheric pressure (AP) and moderate gas temperatures under non-equilibrium plasma conditions [1–6]. Several different approaches are currently available in plasma jet technology to obtain non-equilibrium plasma conditions at atmospheric pressure [6–11]. These approaches can exploit for instance highly asymmetric electrode geometries and sharply curved electrodes (such as in corona discharges), dielectric barriers, sub-millimeter plasma confinement in at least one dimension (i.e., microplasmas) [7–15]. Strategies based on high-frequency plasma excitation are also utilized as in the case of radiofrequency (RF) or microwave (MW) driven discharges [6,9]; while, recently, nanosecond pulsed power supplies have been proposed to achieve strong and stable non-equilibrium plasma conditions [11].

The distinctive feature of plasma jets resides in the fact that the plasma, generated remotely within the device, can be launched outside its physical boundaries, extending in the open space in the form of a so-called "plasma plume" (see the general plasma source scheme in Fig. 1). The adequate choice of the source design, the electric field geometry and gas flow conditions can allow the plasma plume to propagate through the external environment as far as a few tens of millimeters from the device exit [1,3,4].

Atmospheric pressure plasma jets were firstly developed as thermal arc-based plasma sources (i.e., arc jets and plasma torches) [6,8,16], with application in propulsion, cutting, welding and other high-temperature inorganic material processing technologies [8]. Non-equilibrium plasma jet devices began to emerge in the 1990s [2,17,18], benefiting from both the technological advances in the field of non-equilibrium plasma generation at atmospheric pressure, and the rising industrial demand for cold plasma technology in surface processing. Since then a large variety of devices has been developed, differing in the strategy

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http://dx.doi.org/10.1016/j.surfcoat.2017.05.027
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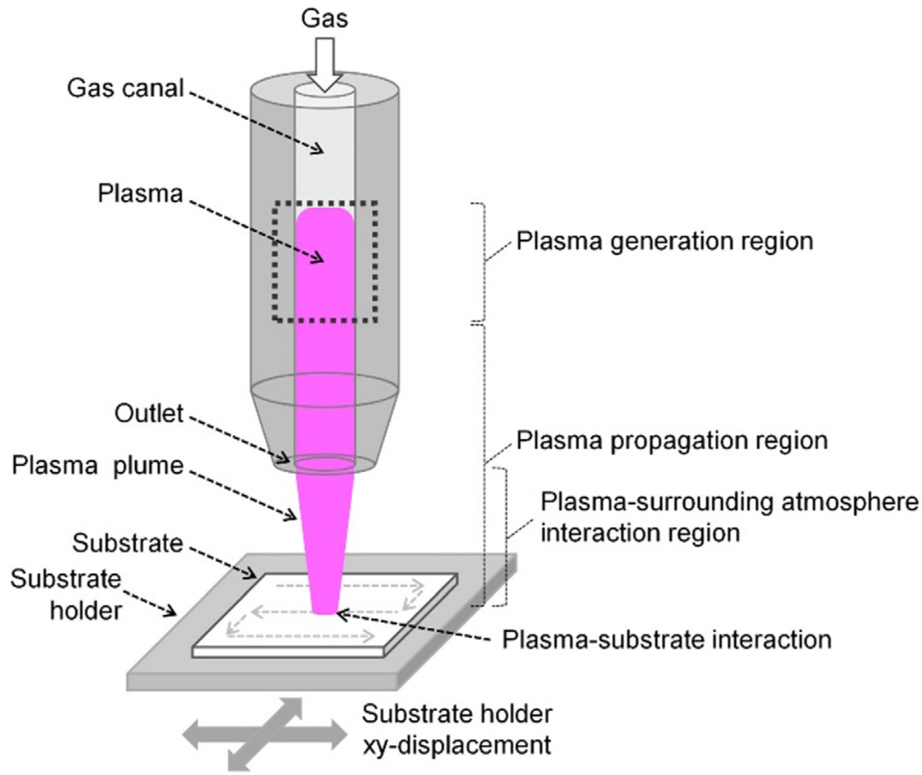

Fig. 1. Schematic diagram depicting a general plasma jet device that can be used in surface processing. Some of the most important issues addressed in this paper are summarized, e.g., the plasma generation and propagation, the plasma interaction with the surrounding environment and the substrate, the surface modification of a localized region of the substrate, the enlargement of the treated area through displacement of the sample holder.

utilized for non-equilibrium plasma generation, in the electrode arrangement and overall architecture as well as in the shape, size and dynamics of the plasma plume ejected from the device [3,4,6].

Over the years, AP non-equilibrium plasma jets have demonstrated to be very promising in a plethora of cold plasma-based processes which allow the surface modification of a large variety of materials, without affecting their bulk properties [19]. These processes can be broadly divided into three main classes [20]:

(i) *Plasma etching* allows the removal of either the substrate material (in both isotropic and anisotropic fashion) or surface contaminants (i.e., *plasma cleaning*) to form volatile products.

(ii) *Plasma-assisted deposition* affords the preparation of organic, inorganic and hybrid multicomponent thin films (average thickness ranging from some nanometers to a few microns) as well as localized structures (width ranging from a few tens to a few hundred microns and height up to several hundred microns). Different approaches can be used such as the plasma-enhanced chemical vapor deposition (PECVD), the aerosol-assisted plasma deposition (AAPD) and various evaporation- and/or sputtering-based techniques [11,15,21].

(iii) *Plasma treatment* consists in the modification of the outermost layers of the substrate through chemical grafting of specific functional groups and/or increase of the crosslinking degree and/or variation of the surface roughness. It includes a wide range of processes utilizing plasmas generally fed with noble gases (e.g., helium or argon) and/or molecular gases (e.g., nitrogen, oxygen, hydrogen and ammonia), operated under experimental conditions that are not able to induce considerable etching and appreciable polymerization.

In addition to the benefits offered by the atmospheric pressure operation, such as the potential cost reduction of plasma reactors as well as the easier handling and maintenance of apparatuses, beyond doubts the main advantage of plasma jets utilization in surface processing is related to their distinctive remote operation. Plasma jets give, in fact, the unique possibility of placing the substrate outside the source physical boundaries, since they are able to bring the plasma, and therefore the reactive plasma species (e.g., radicals, metastables, ions, etc.), in the external environment and even in open air. Consequently, the processing of complex three-dimensional (3D) objects and the integration in existing production lines are much easier. It is worth highlighting that the source physical boundaries are very often mainly dictated by the geometric constraints for the generation of non-equilibrium plasmas at atmospheric pressure. Specifically, typical electrode assemblies utilize narrow gas gaps which are often limited to a few mm (for instance in the case of DBD- and RF discharge-based plasma jets) because of the relatively high breakdown voltage of gases at atmospheric pressure [3,5,7–9]. Microplasma jets impose even more stringent geometric restrictions; however, as miniaturized devices they offer a unique tool towards localized and spatially resolved surface processing at atmospheric pressure [13–15,22–24]. On the other hand, strategies for uniform surface modification over large areas have been also implemented and are currently available in the realm of plasma jet technology [15,25].

However, while appealing, plasma jet technology has the drawback that great efforts are required for process optimization, since many factors can affect the physical and chemical proprieties of the plasma plume propagating in the external environment towards the substrate to be treated. The interaction of the plasma emerging from the device with the surrounding atmosphere and the substrate (Fig. 1) can be responsible for several phenomena that, while predictable in principle, are very difficult to be handled in practice. Indeed, the control of chemical reactions occurring under non-equilibrium plasma conditions can require more effort when dealing with plasma jets.

Different reviews have been published on plasma jet technology so far [3,4,6,19]. Laroussi and coauthors classified atmospheric pressure non-equilibrium plasma jets according to the power supply frequency range [3], the operational parameters [3] and the type of gas used to