Physics Letters A ••• (••••) •••–•••

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Characterization of atmospheric pressure microplasma produced from argon and a mixture of argon–ethylenediamine

M. Bashir [a,*], Julia M. Rees [b], S. Bashir [b], William B. Zimmerman [a]

[a] Department of Chemical and Biological Engineering and Kroto Research Institute, University of Sheffield, Sheffield S1 3JD, UK
[b] School of Mathematics and Statistics, Hicks Building, Hounsfield Road, University of Sheffield, Sheffield S3 7RH, UK

ARTICLE INFO

Article history:
Received 22 July 2013
Received in revised form 28 March 2014
Accepted 31 May 2014
Available online xxxx
Communicated by F. Porcelli

Keywords:
Atmospheric pressure microplasma
Glass microcapillary
Properties of Ar and Ar/EDA plasma
Plasma simulations

ABSTRACT

A non-thermal atmospheric pressure microplasma generated from pure argon (Ar) and a mixture of argon–ethylenediamine vapors (Ar/EDA) has been characterized in this study. A sinusoidal power supply operating at 30 kHz was used to excite microplasma in a rectangular borosilicate glass capillary (4×0.4 mm^2). The monomer EDA was mixed with Ar in order to perform plasma polymerization inside the microchannel. The analyses were made by measuring spectroscopic and electrical parameters of the discharge. The effects of EDA mixing on plasma parameters such as electron, excitation and rotational temperatures during the process of surface coating of the microchannel were investigated. These parameters play an important role in the deposition process. The plasma temperatures estimated through spectroscopic measurement were found in the sequence $T_e > T_{exc} > T_{vib} > T_{rot}$, which indicated the non-thermal characteristics of the proposed DBD microplasma. The parameters of the Ar discharge were also numerically computed using plasma simulations. The numerical predictions of electron temperature (2D simulations) and electron density (3D simulations) were found to be in close agreement to those estimated through experiments.

1. Introduction

Plasmas are produced when energy supplied to a neutral gas converts the gas molecules into charged carriers such as electrons, ions, radicals and excited atoms. Electrons and photons possessing sufficient energy produce ions and further electrons on collision with neutral atoms and gas molecules. This process is known as electron impact ionization or photo-ionization. Several different methods exist for supplying the necessary energy to a gas in order for plasma generation to occur, for example, thermal energy, gas heating by adiabatic compression or excitation by energetic beams. The cheapest and most commonly used method for producing and sustaining plasma on commercial and laboratory scales is the application of an energetic electric field to a neutral gas. There will always be a few pre-existing electrons and ions in the neutral gases that were formed by natural phenomena such as cosmic rays or radioactive radiation. When an energetic electric field is applied to a neutral gas, these pre-existing charge carriers are accelerated which leads to the occurrence of further ionizations. This eventually results in an avalanche of charge carriers and the breakdown process of the gas ensues which is associated with the generation of a steady state plasma [1,2].

Plasma can be generated by several different methods, e.g. glow discharge in a vacuum, DC discharge, atmospheric pressure corona and dielectric barrier discharge (DBD) [3,4]. In DBD plasma generation, one or both electrodes are covered with a dielectric material. DBD plasma is a special type of AC or radio frequency (rf) discharge in which the dielectric barrier straddles the transition from glow to arc at atmospheric pressure. The type of plasma in which the distance between two electrodes is of microscale (<1 mm) is called microplasma. When a discharge is confined to a small scale, its properties for example electron temperature, electron density, gas temperature and photo emission, are typically changed compared to the properties of the conventional plasmas. Therefore, the microplasma parameters for carrying out thin film deposition or surface treatment will be different from those of conventional large scale plasmas. Hence, it is important to understand the properties of microplasma in order to control surface properties of materials for different applications. Plasma polymerized EDA can produce amino functional surfaces which have potential bio applications. For example, amino functionalized plasma polymerized surfaces can be used for covalent immobilization of trypsin (proteolytic enzyme) [5], the enzyme glucose oxidase (GOD) [6]

* Corresponding author.
E-mail addresses: ranabashir77@gmail.com (M. Bashir), j.rees@shef.ac.uk (J.M. Rees), shazia@pieas.edu.pk (S. Bashir), w.zimmerman@shef.ac.uk (W.B. Zimmerman).

http://dx.doi.org/10.1016/j.physleta.2014.05.049
0375-9601/

and the covalent immobilization of heparin for improvement of hemocompatibility [7]. The microchannels coated with bioactive amino functional groups could be further used for a number of bio applications such as on-chip enzyme immobilization and protein separation. We have recently used plasma polymerized EDA for hydrophilic surface modification and functionalization of PDMS microchannel [8].

DBD plasmas produced in small capillaries are very useful for inner surface modification of microchannels because a reactive plasma with high densities of ions and radicals can be sustained at atmospheric pressure without requiring the use of an expensive vacuum chamber. Recent studies on surface modification of sealed microchannels or microcapillaries using atmospheric pressure microplasma include that of Priest and co-workers. They successfully modified the surface of a PDMS microchannel by injecting molten gallium electrodes during the device fabrication and localizing the microplasma to spatially control the surface treatment [9]. Klages et al. [10] treated the inner surface of a sealed microchannel using a pair of externally attached electrodes. Yoshiki et al. [11] reported the deposition of titanium dioxide thin film on the inner surface of a quartz tube using atmospheric pressure microplasma. Surface modification of the inner walls of microchannels is vital for a number of microfluidic and lab-on-chip applications. Since a stable microplasma can be produced at atmospheric pressure for cleaning and surface modification of microchannels, investigations of the physical properties of microplasma generated in a glass capillary tube are essential in order to improve its characteristics.

The Langmuir probe diagnostic technique has been widely used for measuring plasma parameters at low pressures [12,13]. However, this conventional method is not appropriate for characterizing atmospheric pressure plasmas due to their collision dominated behavior. For atmospheric pressure plasmas the mean free path for electrons becomes much shorter than the probe dimension and the probability of an electron–neutral collision occurring increases before an electron is collected by the probe [14]. Also, the immersion of a probe into such plasmas may disturb their normal operation. Optical emission spectroscopy (OES), being a non-invasive and in situ measurement method, offers an alternative approach for characterizing atmospheric pressure plasmas [15,14]. OES provides useful information on different excited states in plasma. It is capable of measuring rotational, vibrational, excitation and electron temperatures without perturbing the state of the plasma.

In this paper, an original study for investigating atmospheric pressure microplasma ignited in a glass capillary tube using pure Ar and Ar/EDA is presented. Ar/EDA plasma was produced to perform polymerization in capillary and is characterized here for the first time. The aim is to characterize and prove the capability of atmospheric pressure discharge for thin film deposition when the distance between two electrodes is of micrometer scale. The paper is structured as follows. The experimental setup is described in Section 2.1. Spectroscopic measurements are described in Section 3.1 and electrical characterization is discussed in Section 3.2. Numerical simulations of DBD microplasma are presented in Section 3.3 and the conclusions of this study are drawn in Section 4.

2. Methods

2.1. Experimental setup for characterizing microplasma

The experimental setup used for generating microplasma in a borosilicate glass microcapillary has been described in detail in our previous studies [16]. A similar setup was used here for characterization of the plasma. In brief, the setup consisted of two flow meters to control the flow rate of argon (Ar) gas (0–6 L min^{-1}) and Ar containing the ethylenediamine vapors (0-30 ml min^{-1}).

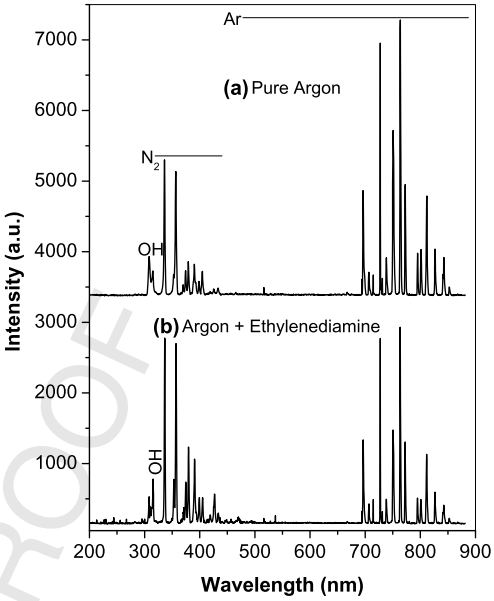

Fig. 1. Optical emission spectra recorded for microplasma generated at a power of 15 W, (a) pure argon and (b) argon mixed with vapors of ethylenediamine. A monomer solution of ethylenediamine was vaporized at 75 °C and argon gas with a flow rate of 10 sccm was bubbled through it.

Table 1
Spectroscopic data of ArI emission lines selected for estimating excitation and electron temperatures.

Wavelength (λ_{ij}) (nm)	E_i (eV)	g_i	A_{ij} (10^8/s)	Transition
516.22	15.31	3	0.00914	6d → 4p
537.34	15.46	5	0.00555	7d → 4p
693.76	14.69	1	0.0317	4d → 4p
714.7	13.28	3	0.00643	4p → 4s
727.29	11.62	3	0.0183	4p → 4s
731.17	14.84	3	0.0177	6s → 4p
750.38	13.48	1	0.472	4p → 4s

E_i, g_i and A_{ij} denote the excitation energy, statistical weight of the emitted upper level i, and the transition probability of spontaneous radiative emission from the upper level i to the lower level j, respectively.

The DBD microchip was constructed from a rectangular borosilicate glass capillary tube (0.4 × 4 mm). The electrodes were made from two aluminium sheets having dimensions 75 × 3 × 0.5 mm^3 ($L \times W \times H$). The electrodes were attached in parallel along the rectangular glass capillary tube. The upper electrode contained a circular hole of diameter 2 mm for transmitting plasma light via a fibre optic cable to the spectrometer. The emission spectra of micro-discharge were recorded using a USB2000 photospectrometer (Ocean Optics) in a UV-visible spectral range (200–900 nm). A fibre optics cable suitable for the UV-visible range was used for collecting light emitted from the plasma. The spectra were recorded using a spectra suite software package (Ocean Optics). The integration time selected for spectroscopy was varied from 300–1000 ms and the boxcar width was set from 0–4 in order to optimize the intensity and noise ratio of the spectrum.

3. Results and discussion

3.1. Spectroscopic measurement

Atmospheric pressure microplasma generated in a capillary microchip has been characterized using optical emission spectroscopy. In a non-thermal plasma the species such as neutral atoms, ions, radicals and electrons have different energy states. The temperature of the plasma affects the distribution of these energy