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Near cathode optical emission spectroscopy in N_2–H_2 glow discharge plasma

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Abstract

Optical emission spectroscopy (OES) is a non-intrusive diagnostic technique, widely used to study different kinds of plasmas. In the present work, a locally resolved OES technique was used to obtain near cathode (substrate) emission spectra for N_2–H_2 glow discharges. It was observed that, along with N_2^+ and N_2 lines, the characteristic atomic nitrogen lines at 742.3 nm ($3p\ ^4S^0_{3/2} \rightarrow 3s\ ^4P_{1/2}$), 744.2 nm ($3p\ ^4S^0_{3/2} \rightarrow 3s\ ^4P_{3/2}$), 746.8 nm ($3p\ ^4S^0_{3/2} \rightarrow 3s\ ^4P_{5/2}$) and H_α (656.3 nm) were the main emissions coming from the sheath region that shrouded the cathode. A qualitative analysis of the spectral lines near the cathode has been done in order to understand the mechanism of plasma nitriding and the role played by the hydrogen in the nitriding process. The decrease in local intensity of these atomic lines with hydrogen composition suggests that the effect of hydrogen is to enhance the sticking/adsorption of N on the cathode surface.

Keywords: Optical emission spectroscopy; Spectral intensity; Adsorption; Cathode sheath; Plasma nitriding

1. Introduction

The N_2–H_2 discharges have been intensively investigated in order to understand interaction of the discharge plasma with cathode (substrate) surface, for studying material modification, formation of various metal-nitrides and subsurface diffusion of nitrogen. Plasma nitriding is one of the widely used surface modification plasma process. The properties of the plasma nitrided surface depend on the N_2 and H_2 gas ratio [1–9]. Several models have been proposed to explain the plasma nitriding process [1–5]. It was suggested that the N_2^+, N^+ and NH_x^+ ions were the active species in the nitriding process [1,3]. In these models [1,3] it was proposed that the primary role of hydrogen is to assist the generation of atomic nitrogen by dissociation of NH_x^+ at the cathode surface. However, an experiment was performed to show that the ions ware not essentially required for plasma nitriding. Pure Fe and steel samples were nitrided principally by neutral nitrogen atoms [2,5].

The role of hydrogen was generally attributed to the enhancement of the nitrogen atom diffusion by removal of the surface oxides [10]. The increase of discharge current has been associated with high secondary electron yield in presence of hydrogen [2,3,5], though it is not established for plasma nitriding conditions. However, in a detailed theoretical study of N_2–H_2 discharges it was shown that with addition of H_2 in pure N_2 discharges, the tail of the electron energy distribution function (EEDF) increased [11–14]. This increase of electron temperature caused higher ionization rate than the pure nitrogen discharges. In addition to this, the collisional interaction of the discharge electrons with the excited electronic states of N_2 with H_2 and NH_x species might also enhance the discharge [11,12]. Further, the process of nitriding was modeled assuming that the hydrogen increases the surface sticking coefficient of nitrogen, which is followed by nitrogen diffusion into cathode subsurface [4]. This model did not have any direct experimental evidence and contradicted the experimental observation of nitriding [1].

Despite these efforts, there are issues that remain unresolved. There are questions regarding the most dominant species responsible for plasma nitriding and their availability at the cathode surface, the effect of hydrogen on the substrate surface and how the presence of H_2 aids the plasma nitriding process. The crux of this paper is to identify active species at the metallic cathode surface, and address some of the issues mentioned above. This was done using a locally resolved OES technique which can isolate the

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emissions from the sheath region, excluding the emissions from negative glow region, of a dc glow discharge.

In the next section experimental arrangement is described in detail. The spectra observed for pure N_2 discharges are given in Section 3 and for N_2–H_2 discharges given in Section 4. In Section 5, the main channels for the atomic nitrogen generation are listed. The energetic neutral generation, effect of hydrogen on emission intensity and the dependence of dissociative chemisorption of N_2 on translational energy are discussed in Section 6. In the final section the important findings of the present investigation is summarized.

2. Experimental set-up

The experiments were performed in a discharge chamber made up of SS 304 with an internal diameter of 30 cm and length of 40 cm. The cathode was a SS disc with diameter of 40 mm and thickness of 10 mm fixed on a tip of J-type thermocouple, and was biased to −600 V. The chamber wall was connected to the power supply ground and acted as anode. The experimental set-up is shown in Fig. 1. The system was pumped down to a base pressure ~ 10^{-3} mbar using a rotary pump. The digital capacitance manometer (CMR 263) gauge was used to measure the pressure inside the chamber. The chamber was filled with N_2 and H_2 gas (99.999% purity) through a precision dosing valve (Balzer make). Prior to filling the gases into the chamber through dosing valve, the gases were mixed in the desired ratio by N_2 and H_2 mass flow controllers (MFCs) into a plenum. Each of the MFCs (Alborg make, GFC 17) has a flow range of 0–500 mL/min.

The emissions from the discharge were recorded using an optical set-up, that consisted of a 1 m imaging spectrograph (ARC make) with a grating of 1800 lines/mm, attached with a CCD (1024×256) having 24 μm pixel size. For all the recordings, the slit was open to 50 μm and the achievable wavelength resolution at these settings was ~0.025 nm. The emissions were collected simultaneously using two types of light collecting systems (LCS), through optical fiber F1 and F2. The LCS (F1) comprised of a Bk-7 Plano convex lens (diameter 50 mm, 150 mm focal length) and silica fiber of 1 mm core diameter (numerical aperture: 0.22). The view subtended by this LCS was normal to the discharge column grazing the surface of the cathode and always collected radiation from a fixed location.

The second light collecting system (F2), mentioned as MOP (Moving Optical Probe) in this paper, consisted of a silica fiber inserted through a 6 mm SS tube. The SS was covered with a 1 mm thick, chemically inert and insulating Borosil glass tube protecting the fiber tip. The MOP was kept floating and drew no current. We have assumed that the effect of MOP on plasma was marginal and can be ignored. The MOP enabled collection of radiation locally. It could be moved either towards or away the cathode. When the MOP was positioned very near to the cathode i.e. inside the ion sheath, it collected emissions only from the cathode surface. For the present experimental parameters the sheath thickness was ~4.2 mm [15,16]. In order to record the emission spectra of the species near the cathode surface, excluding emissions from negative glow and positive column, the tip of the MOP was placed at a distance 3 mm away from the cathode surface. This distance (3 mm) was established by sampling the spectra at different distances from the cathode surface for all N_2–H_2 composition such that no emission was collected from negative glow region.

3. The optical emission spectra of N_2 discharge

The intense spectral lines observed in the present discharge conditions are listed in Table 1. The OES spectra are shown in the following figures. In Fig. 2, the spectra of pure nitrogen discharge,

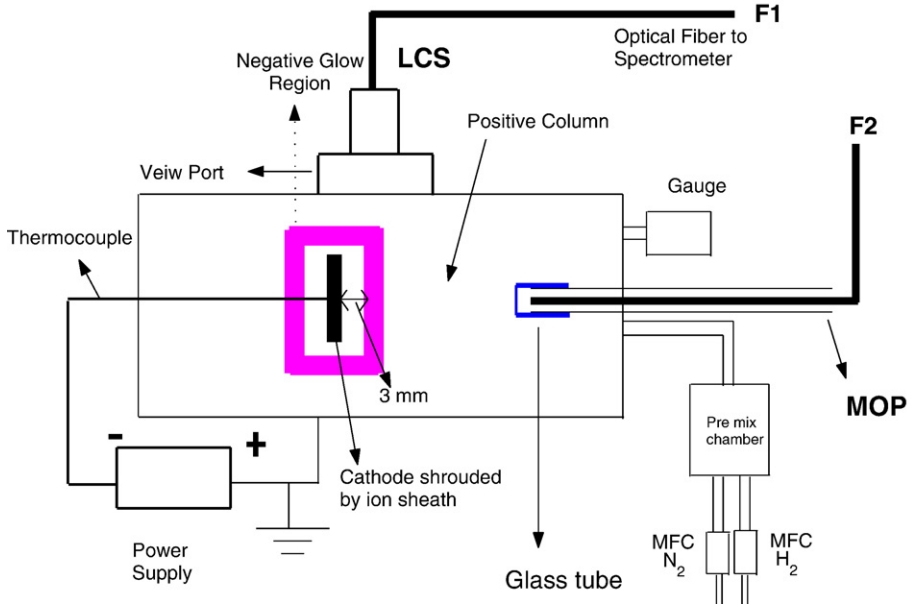

Fig. 1. (Color online). The experimental set-up consists of two optical fibers F1 (LCS) and F2 (MOP). The MOP can be moved on the axis normal to the cathode surface. The LCS was fixed at a distance of 14 cm from the cathode. The data from both optical fibers was simultaneously recorded. The thickness of sheath was ~4.2 mm and the negative glow region shrouding cathode is shown. When the MOP was placed at a distance 3 mm from the cathode surface it excludes the emissions coming from negative glow and positive column.