

STUDY OF TITANIUM EMISSION SPECTRA IN N₂ – H₂ ABNORMAL DC GLOW DISCHARGE

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Abstract. In this paper we tried to answer why small amount of hydrogen (3 %) in a nitrogen abnormal glow discharge so strongly reduce Ti I spectral line intensities. Decreasing of Ti I line intensities in N₂ – H₂ discharge are compared with less pronounced decreasing of N I line intensities. Using emission spectroscopy we have observed that line intensity changes are correlated to variations in electron energy distribution function (EEDF) and change of metastable density.

1. INTRODUCTION

Discharges in N₂–H₂ mixtures have been intensively investigated to understand the physical and chemical processes in nonequilibrium, low-temperature plasmas (Garscadden and Nagpal 1995, Guerra et al. 1997, Gordiets et al. 1998) and also for applications in plasma chemical treatment of materials (Ricard et al. 1998). Our work with N₂–H₂ discharge was not motivated by the mentioned field of interests. Our intention was to investigate an interesting observation given in Wronski's paper (Wronski 2000). Namely, Wronsky has noticed that traces of hydrogen in nitrogen carrier gas extinguish emission of Ti lines in a normal glow discharge with titanium cathode. In our spectroscopic studies of an abnormal glow discharge, of the Grimm type (Grimm 1967, 1968) in nitrogen, the decrease of titanium line intensities is noticed whenever hydrogen is mixed with nitrogen. Here we draw attention to the fact that discharge conditions in (Wronski 2000) $p = (0.13 - 0.47)$ mbar, $j = (0.1 - 0.5)$ mAcm⁻² and $U = 3000$ V, are quite different from ours, $p = 4$ mbar, $j = (10 - 42)$ mAcm⁻², $U = (800 - 2000)$ V.

When considering the decrease of Ti I line intensities in a glow discharge with N₂ - H₂ gas mixtures and Ti cathode, one may use two possible explanations: Change of Electron Energy Distribution Function (EEDF) or/and change of number density of molecule and atomic nitrogen in metastable states.

2. EXPERIMENTAL SETUP

Our discharge source, a modified Grimm type glow discharge, is laboratory made after Ferreira *et al.* (1980) and described in details elsewhere (Kuraica *et al.* 1992). Here, for completeness, minimum details will be given. The hollow anode, 30 mm long with inner and outside diameters 8.00 and 13 mm, has a longitudinal slot (15 mm long and 1 mm wide) for side-on observations along the discharge axis. The water-cooled cathode holder has exchangeable titanium (purity 99.5%) electrode, 18 mm long and 7.60 mm in diameter, which screws tightly into its holder to ensure good cooling. A gas flow of about 100 cm³/min of nitrogen (purity 99.995%) or nitrogen-hydrogen mixture (N₂ + 3.0% H₂) is sustained at a pressure of 4.0 mbar. To run the discharge a 0 – 2.5 kV voltage stabilized power supply is used.

Spectroscopic observations of the discharge are performed in two directions: along the axis (end-on) and perpendicular to the discharge axis (side-on) through longitudinal anode slot. For the end-on observations, 1 m spectrometer equipped with one-dimensional CCD detector is used. The end-on spectra represents the integral intensities along the observation path. For a discussion on the change of line intensity, it is very important to know, even approximately, value of reduced electric field, E/N , in a region of sputtered atoms excitation. The end-on observation gives integral intensity from regions with varying E/N . To overcome this drawback of end-on observation, the side-on intensity distributions along the discharge axis are recorded as well. For side-on spectra recording of the discharge through the anode slot 0.3 m monochromator with a photomultiplier was used.

3. RESULTS AND DISCUSSION

In the presence of hydrogen in nitrogen discharge the large intensity reduction of all Ti I lines is always detected, while the change of N I line intensity is not so significant, see Fig. 1a. In our experiment, addition of hydrogen in the glow discharge leads to the change in discharge voltage and current. Thus, in order to demonstrate the influence of hydrogen presence in the nitrogen on the intensity of Ti I and N I lines in Fig. 1, the voltage is kept constant.

Fig. 1a shows how the intensity ratio I_M/I_N , where I_M and I_N are intensities of spectral lines in N₂ + 3%H₂ mixture and in pure N₂, depends on atomic upper energy level for titanium and nitrogen atoms. The atomic lines that were selected are relatively strong and isolated. (Striganov and Sventickij 1966). Line intensities are presented without correction to the discharge parameters. However, the voltage is kept the same. Intensity ratio of titanium lines is strongly dependent on upper energy levels for the energies below 2.5 eV, and it has a minimum value for the recorded line with the lowest upper energy level. It increases with energies of upper levels. At energies between 3.2 eV and 3.9 eV intensity ratio has, within a region of experimental error, almost constant value. Metastable levels of atomic nitrogen N(²D) at 2.38 eV and N(²P) at 3.58 eV are shown at Fig. 1a. Widths of

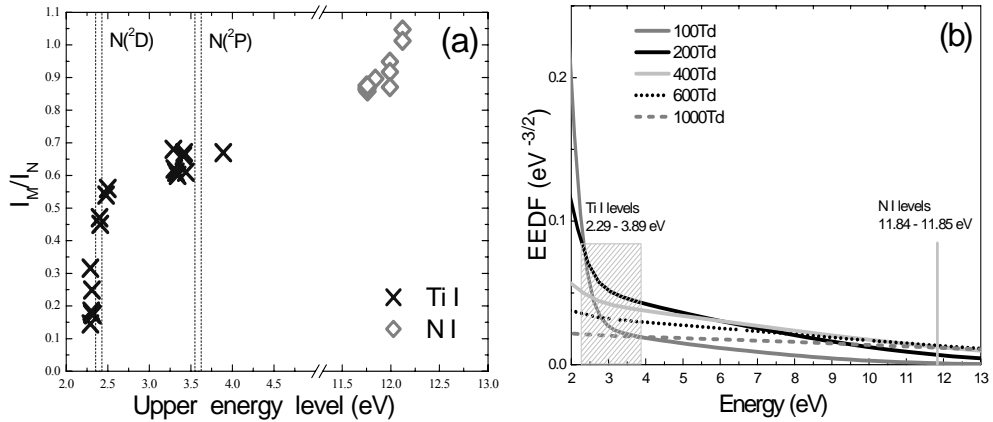


Figure 1: (a) Intensity ratio vs. Upper energy level for Ti I and N I lines. I_M – Intensity in N₂+3%H₂ mixture, I_N – Intensity in pure N₂. (b) EEDF calculated for several values of E/N (1 Td = 10⁻¹⁷ Vcm²). Energy of upper levels for Ti I and N I lines is marked on the graph.

stripes, which are used to assign metastable levels, are determined by gas temperature, which in the nitrogen discharge is about 600 K, according to the measurements of rotational temperature (Majstorović et al. 1999).

For a discussion on the change of line intensity, it is very important to know the axial intensity distributions, because they may give, even approximately, information on the EEDF in the discharge. Especially comparison of normalized axial intensity distributions (NAIDs) may show change of the EEDF. Fig 2a shows NAID of Ti I 519.30 nm (0.02 – 2.41) eV line intensities for different discharge

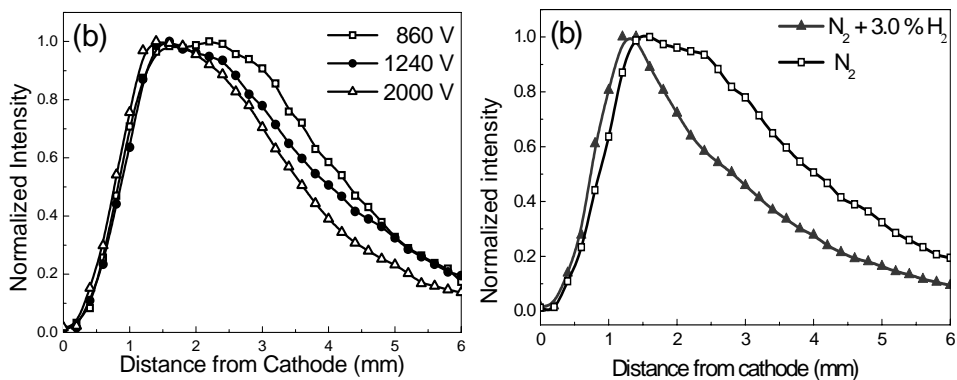


Figure 2: (a) Normalized axial intensity distributions of Ti I 519.30 nm (0.02 – 2.41 eV) line for different discharge voltages in pure nitrogen. (b) Normalized axial intensity distributions of the same Ti line intensities in N₂ and N₂ + 3 %H₂. Voltage: 1240 V.

voltages in pure nitrogen. Analyzing these graphs two conclusions can be made: with increasing voltage NAID became narrower and shifted towards the cathode. On the other hand, increasing the discharge voltage evidently changes the EEDF, so narrowing of NAID is directly connected with a change of the EEDF by increasing E/N (Obradović *et al.*).

It is already recognized that addition of small amount of hydrogen in nitrogen DC discharge changes EEDF in such way that E/N and mean electron energy increase (Garscadden and Nagpal 1995). This means decreasing of concentration of low energy electrons (responsible for excitation of Ti I levels) and consequently decreasing of intensities of Ti I lines. Analyzing the EEDF, calculated for nitrogen using code BOLSIG+ (Hagelaar and Pitchford 2005), it may be concluded that in the lower energy region influence of E/N on the slope of EEDF is very strong, see Fig. 1b. This explains why the decrease of Ti I line intensities are larger for the electronic levels with lower energy.

On the other hand, change of EEDF with addition of hydrogen influences on decreasing of N(²D) metastable concentration, which is excited by electronic excitation from N(⁴S) ground level. Since level N(²D) is energetically close to Ti I levels Penning excitation is plausible, so decreasing of metastable concentration, decreases intensity of Ti I lines. Addition of hydrogen also decreases N(²D) metastable concentration through quenching. Namely, coefficients for quenching of N(²D) with H₂ are ~ 100 times greater for quenching by N₂ (Gordiets *et al.* 1998).

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