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A spectroscopic study into the decomposition process of titanium isopropoxide in the nitrogen–hydrogen 100 kHz low-pressure plasma

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Abstract

Optical emission spectroscopy was employed for the study of the nitrogen–hydrogen and nitrogen–hydrogen–titanium (IV) isopropoxide mixtures in the 100 kHz low pressure capacitively coupled discharge. High-energy species were identified in the plasma phase. The behavior of the excited species versus the gas composition has also been investigated. The optical actinometry technique was applied in order to evaluate the N_2, CH, CO, CN, N, C and the H relative concentrations versus the hydrogen concentration in reactive mixtures. The effect of the hydrogen concentration in the nitrogen–hydrogen mixture on the decomposition processes of titanium isopropoxide was investigated. The plasma temperature (the H excitation temperature, the CN, N_2 and N_2^+ vibrational temperatures and the N_2^+ rotational temperature) as well as the electron number density were determined here. The temperature magnitudes ($T_{exc} \approx 5700$–7400 K, $T_{vib}(CN) \approx 4700$–8100 K, $T_{vib}(N_2) \approx 2700$–$3050$ K, $T_{vib}(N_2^+) \approx 1500$–$1600$ K and $T_{rot}(N_2^+) \approx 660$–$890$ K) indicated a very significant deviation from the LTE state.

Keywords: Plasma diagnostics; Optical emission spectroscopy; Plasma-assisted chemical vapor deposition; Titanium isopropoxide

1. Introduction

The plasma-assisted chemical vapor deposition (PACVD) methods, using the easy volatile metal organic compounds (MO)-PACVD, are widely applied for the production of many kinds of coatings and thin layers [1]. Among them, titanium nitride (TiN) and thin layers of titanium carbon nitride (TiCN, TiCNO) are very interesting as regards their mechanical, electrical, anticorrosive and decorative properties [2–4].

Normally, titanium chloride ($TiCl_4$) is applied for the production of TiN or TiCNO coatings (e.g. [4–8]). However, chlorine impurities may affect the properties of the thin layers [3]. Alternatively, easy volatile MO, such as titanium tetraisopropoxide (TIP) [3,9–11], tetrakis dimethylamidotitanium (TDMAT) [12,13], tetrakis diethylamidotitanium (TDEAT) [3], diethylaminotitanium (DEAT) [14], dimethylaminotitanium (DMAT) [15], have been used recently to deposit titanium nitride or thin layers of titanium carbon nitride. Weber et al. [2,9] have shown that thin films of high quality TiN are produced from titanium (IV) isopropoxide–nitrogen microwave plasma at a low substrate temperature. Multi-component TiCNO layers were also produced [10,11] from the direct current (dc) TIP–N_2–H_2 plasma on the Armco-iron steel.

In order to understand the plasma chemistry of the PACVD processes, it is necessary to know the conditions occurring in the plasma phase and the concentrations of species in the excited states as well as in the ground states. The plasma parameters (i.e. the temperature, the concentrations of high energy species, the electron number density) are very important from the point of view of the processes leading to the formation of thin layers. The plasma diagnostics may appear very useful for the understanding of the deposition process. Optical emission spectroscopy (OES) as well as optical actinometry, due to their non-invasive character, have been used as tools for plasma diagnostics and for investigating the PACVD processes [1,5,6,16–19]. The OES technique was frequently

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applied in order to study and control the plasma TiN, TiCN and TiCNO deposition processes [3–6,8,10,18]. However, only a few papers are concerned with the investigation of the MO-PACVD processes by means of OES in system containing titan MO. Boo et al. [3] analyzed the radical formation and ionization behaviors in plasma containing tetrakis diethylamidotitanium by means of OES. Wierzchon and Sobiecki [10] investigated the emission spectra of selected species, i.e. CN, Ti, Ti^+, versus the cathode temperature in the dc titanium isopropoxide plasma. In their earlier work, Kulakowska-Pawlak and Zyrnicki [18] studied the dc glow discharge in the reactive mixture containing titanium isopropoxide. They found that emission intensities of active species were sensitive to changes in the plasma gas composition and the cathode temperature.

The main aim of this work is to obtain information on the decomposition process of TIP in the mid-frequency nitrogen–hydrogen plasma, while the former studies [10,18] concerned the dc discharges. The glow discharges in the nitrogen–hydrogen–TIP and in the nitrogen–hydrogen mixtures were characterized by OES as well as by the optical actinometry technique. The plasma parameters, i.e. plasma temperatures (excitation, vibrational and rotational) and electron number density at various mixture compositions were also investigated.

2. Experimental setup

Mid-frequency power supply (100 kHz, 100 mA, 200 W) was employed here to generate low-pressure plasma in the reactive mixture. The plasma was excited in a Pyrex glass cylindrical reactor chamber between two parallel Armco-iron electrodes (diameter: 22 mm, thickness: 2 mm, distance between the electrodes: 16 mm). The chamber had water cooled walls and a quartz window enabling observation of the plasma radiation spectrum. A schematic diagram of the experimental setup was described in the earlier work [17].

Titanium (IV) tetraisopropoxide (chemical formula $Ti[OCH(CH_3)_2]_4$, purity 97%, purchased from Aldrich-Sigma) was introduced by means of a bubbler system to the plasma reactor with a stream of gases. The evaporation temperature of TIP (60 °C) was controlled with the aid of the thermostat. The gas line connecting the bubbler system with the plasma reactor was additionally heated to about 60 °C in order to avoid the condensation of a titanium MO on the cold walls of the pipeline. The flow rate of TIP was constant and kept at the level of $0.04\,g\,min^{-1}$ ($140\,\mu mol\,min^{-1}$).

A mixture of nitrogen and hydrogen was used as a carrier gas. The percentage of hydrogen in the mixture was as follows: 0, 25, 50, 75 and 100. The flow rate of reactive gases was regulated with the aid of flow meters (Tylan General). The pressure was kept constant (532 Pa) and controlled by means of a pressure gauge (Pfeiffer). The gas mixture was pumped continuously by a rotational pump device. A cryogenic trap (liquid nitrogen) in the front of vacuum pump system was additionally applied.

The radiation emitted by the plasma was measured by a JY TRIAX 320 ($f = 32$ cm, resolution 0.050 nm) monochromator and a high resolution PGS-2 spectrometer ($f = 200$ cm, resolution 0.015 nm) with photomultiplier tubes: Hamamatsu R-928 and Hamamatsu DH-3, respectively. A quartz achromatic lens was applied to focus the plasma radiation into the entrance slits of the monochromator/spectrometer. The sensitivity of the optical systems versus the wavelength was calibrated with the aid of the Bentham halogen lamp (the Protection Engineering Ltd. certificate in the 250–800 nm spectral range).

3. Results and discussion

3.1. Identification of plasma components

The spectra of N_2–H_2 and N_2–H_2–TIP were measured in the range of 200–800 nm wavelength. The identification of atoms and diatomic molecules was carried out with the aid of the NIST Atomic Spectra Database [20] and the Pearce and Gaydon molecular spectra table [21]. Numerous bands of N_2 (strong $C^3\Pi_u$–$B^3\Pi_g$ system and weak $B^3\Pi_g$–$A^3\Sigma_u^+$ system) and strong bands of N_2^+ ($B^2\Sigma^+$–$X^2\Sigma^+$ system) were detected in the N_2–H_2 plasma. The most intense spectra were the (0–0) bandhead of the N_2^+ ($B^2\Sigma^+$–$X^2\Sigma^+$) system and the (0–2) and (0–0) bands of N_2 of the $C^3\Pi_u$–$B^3\Pi_g$ system. Strong hydrogen lines (H_α at 656.28 nm and H_β at 486.13 nm) were observed. The next hydrogen line, i.e. H_γ at 434.14 nm was not clearly identified due to the overlapping by the $C^3\Pi_u$–$B^3\Pi_g$ (0–4) band of N_2 at 434.36 nm. Some weak nitrogen lines: the atomic N I at 742.4, 744.2, 746.8 and 818.8 nm and the ionic N II at 500.1, 500.5, 567.6 and 567.9 nm were detected. Additionally, the $A^3\Pi_g$–$X^3\Sigma^-$ (0–0) NH bandhead at 336.0 nm, partially overlapped by the strong (0–0) $C^3\Pi_u$–$B^3\Pi_g$ band of N_2 with the bandhead at 337.13 nm was also noticed.

The introduction of evaporated TIP into nitrogen–hydrogen plasma zone resulted in the emission of CN spectra (the most intense bands of the violet system $B^2\Sigma^+$–$X^2\Sigma^+$ and very weak of the red system $A^2\Sigma$–$X^2\Sigma$), CO (the $B^1\Sigma$–$A^1\Pi$ bands at 519.82 nm (0–2), 483.53 nm (0–1) and 451.09 (0–0)), CH ($A^2\Delta$–$X^2\Pi$ (0–0) band at 431.4 nm) (see Fig. 1) and C I line (at 247.86 nm) species. Additionally, the weak spectra of C_2 belonging to the $A^3\Pi_g$–$X'^3\Pi_u$ transition with the band heads at 473.71 nm (1–0), 471.52 nm (2–1), 512.93 nm (1–1) and 516.52 (0–0) and the weak spectra of CO^+ ($B^2\Sigma^+$–$X^2\Sigma^+$) in the 210–250 nm spectra region (the band heads at 211.24 nm (1–0), 218.98 nm (0–0), 229.96 nm (0–1), 232.52 nm (1–2)) were also identified.

In contrast to the emission of spectra of the rf and dc plasmas with $TiCl_4$ [4,5,7,8], we did not observe any atomic and ionic lines of titanium. It indicates that the