CHARACTERIZATION OF CH<sub>3</sub>SiCl<sub>3</sub>/N<sub>2</sub>/H<sub>2</sub> RF PLASMA USING OPTICAL EMISSION SPECTROSCOPY AND ACTINOMETRY

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Abstract

Glow discharges (100 kHz) fed with methyltrichlorosilane-nitrogen-hydrogen mixtures have been the subject of present studies. Optical emission spectroscopy and a dynamic form of actinometry was employed to determine the time-dependent changes in the emission intensities of Si I, CH, CN and in the actinometric concentrations of N<sub>2</sub> and H. The emission measurements were made up to 80 minutes following introduction of CH<sub>3</sub>SiCl<sub>3</sub> to an N<sub>2</sub>/H<sub>2</sub> plasma. Results indicate on rapidly decreasing fragmentation of CH<sub>3</sub>SiCl<sub>3</sub> molecules during the first minutes of the process. Nitrogen strongly enhanced formation of CN and CH radicals.

1. Introduction

There has been much research into the deposition, properties and microstructure of amorphous silicon carbide and silicon nitride thin films. Both materials have attracted increasing interest because of their potential applications in microelectronics and hard-coatings technologies. In an attempt to develop coatings with a wide range of electronic band gap on the one hand and with high wear resistance and hardness on the other hand, amorphous silicon carbide nitride (a-SiC<sub>x</sub>N<sub>y</sub>) thin films have been proposed. However, a number of works dealing with such coating preparation is very limited up to now [1-5].

This work deals with rf plasma of CH<sub>3</sub>SiCl<sub>3</sub>-N<sub>2</sub>-H<sub>2</sub> gas mixture. It appeared interesting to us to study such mixture since it is potential candidate for plasma-enhanced CVD of a-SiC<sub>x</sub>N<sub>y</sub> films. CH<sub>3</sub>SiCl<sub>3</sub> (MTS) is one of the most commonly used precursors for the production of a-SiC films by CVD and PCVD processes. MTS has the advantage of being inexpensive and of decomposing at relatively low temperature.

2. Experimental

The discharge was maintained in a cylindrical, water-cooled glass chamber fitted with horizontal, parallel-plate electrodes connected to a rf (100 kHz) power supply. The distance between the bottom electrode (22 mm diam.) and the upper electrode (12 mm diam.) was about 15 mm. The chamber was pumped continuously. MTS (ABC.R, 95% purity), held in a glass bulb, was cooled in ice-water mixture and admitted, via teflon-valve, to the stream of N<sub>2</sub> and H<sub>2</sub> gases. The Ar (actinometer) admission was controlled by mass flow controller (Tylan General). All the experiments were carried out at a total pressure of 7.3 kPa.

A Bentham M-300HR scanning monochromator (grating 1800 grooves/mm) was installed at the quartz window of the reactor and focused at a position the more intense emission arises from the region close to the bottom electrode. The optical measurements were calibrated on a standard halogen lamp (Bentham).
3. Results and discussion

3.1. N₂ and N₂-H₂ plasma

First experiments were carried out with nitrogen and nitrogen-hydrogen mixtures (without MTS). The N₂/H₂ pressure ratio was 4:1, 3:2 or 1:4. The current density was also changed and was equal 70, 100 or 120 mA. A small fraction of argon (7%) was introduced into the reactor in order to apply the actinometry method. The OES study performed for these simple plasma systems served as a reference for the MTS-N₂-H₂ system analysed further and enabled us to analyse validity of actinometry for H-atoms and N₂ molecules.

The main features of the spectrum emitted by the nitrogen and N₂-H₂ plasmas were the N₂ C'T₁-B'T₁ bands system, the N₂ B²Σ-X²Σ bands system, NH(A-X) band at 336 nm and the Balmer atomic hydrogen emission lines (H₆ 656.3 nm, H₇ 486.1 nm, H₈ 434 nm). The presence of hydrogen lines and NH band in the nitrogen plasma spectrum is caused by the contamination of nitrogen. In addition, many atomic and ionic lines of argon were observed when argon was introduced into the chamber.

In an attempt to understand basic differences between the nitrogen and nitrogen-hydrogen plasmas, the electron densities (nₑ) and temperatures (Tₑ) were evaluated (using emission spectroscopy methods). For the determination of nₑ, the well-established technique using the shape of the H₂ line was selected [6]. The value of nₑ determined such way was put into equation describing the intensity ratio of ionic and atomic line of the same element and assuming LTE, the electron temperature was estimated [6]. The Ar II (459 nm) and Ar I (755.5 nm) lines were used for this purpose. The absolute values for nₑ and Tₑ can be in large error, but variations of these values with experimental conditions can be discerned. In Figs. 1a and 1b, nₑ and Tₑ values are compared for the studied plasmas and current densities. As can be seen, the electron concentration generally increased with current (power) and with rise of nitrogen content in N₂-H₂ mixture.

![Fig.1. Electron density (a) and temperature (b) as a function of the current density.](image)

The nitrogen plasma showed highest nₑ and at the same time, lowest Tₑ, than the hydrogen-containing plasmas. Among these latter, the highest Tₑ values were found for plasma with the lowest nitrogen content (N₂:H₂=1:4). The electron temperature, however, was at about the same 13000 K (1.1 eV) over the whole range of experimental conditions. We also evaluated the vibrational temperature of N₂ molecule using Boltzmann method for the C'T₁-B'T₁, Δv=-2 bands. The results showed that the temperature was about 3000 K for all studied conditions. The excitation temperature, which was determined from the intensity ratios of hydrogen lines (H₆ and H₇) had the values of about 6000 K for the N₂-H₂ plasmas and about 8500 K for the nitrogen plasma. One should therefore conclude that the rise of nitrogen content in the N₂-H₂ discharge mixture caused increase in the electron density, but left practically unchanged the electron energy distribution function.
3.2. Actinometric determination of the atomic hydrogen and nitrogen molecules concentration

The actinometric technique is well established in current literature (e.g. [7]). We used the argon 750.4 nm line as the reference with respect to the H\(\alpha\) and the N\(\alpha\) (371.1 nm) emissions. Figs. 2a and 2b show the H\(\alpha\) intensity and the normalized intensity (I\(\alpha\)/I\(\alpha\)) respectively, as a function of current for the different plasmas studied. As can be seen, while there was no systematic trend in the behaviour of the H\(\alpha\) intensity with current and hydrogen content, the normalized intensity increased when rf current and hydrogen content increased. Actinometry compensates for changes in the electron density (or energy). Assuming the corona model to the plasma and that excited H atoms are produced directly from the ground electronic state [7], the intensity ratio I\(\alpha\)/I\(\alpha\) should be proportional to the hydrogen electronic ground state concentration. As for both lines, H\(\alpha\) and N\(\alpha\) (not shown) the normalized intensities were found to be proportional to the amount of hydrogen introduced, we conclude that actinometry can be applied for getting information concerning the tendencies of variations of H-atom mole fraction as the function of operating conditions. The results presented in Fig. 2b, indicate an increase of H-atom mole fraction with current (power density). It can be attributed to an increase of efficiency of electron-impact H\(\alpha\) dissociation and/or to thermal dissociation of molecular hydrogen.

![Graphs showing relative emission intensity of H\(\alpha\) and normalized emission intensity of H\(\alpha\) as a function of current density.]

Fig. 2. Relative emission intensity of H\(\alpha\) (a) and normalized emission intensity of H\(\alpha\) (b) as a function of the current density.

The variations of k\(\alpha\) and I\(\alpha\)/I\(\alpha\) were very similar. A good linear dependence between the normalized intensity and the N\(\alpha\) fraction in the feed were found. The slope of the corresponding straight lines was the same for different current densities. The above result constitute a proof for the validity of actinometry for N\(\alpha\) molecules under this set of experimental conditions.

4. MTS-N\(_2\)-H\(_2\) plasma

In the optical spectrum emitted by MTS-N\(_2\)-H\(_2\) plasma were identified all the N\(_2\), N\(_2^{-}\), NH transitions and the H lines observed for the N\(_2\)-H\(_2\) plasma. Additionally appeared: Si I lines (251.4, 251.6, 252.4, 252.8, 288.1 nm), Si II lines (634.7, 637.2 nm), the CH (A'\(\Delta\)-X'\(\Pi\)) band-head at 431.4 nm and the violet band system of CN (B'\(\Sigma\)-X'\(\Sigma\), \(\Delta\nu=0\)). An increase in the supply of MTS resulted in emission of the SiCl spectrum (near 281 nm) and the SiCl\(_2\) continuum at 330 nm. At the same time, the discharge conditions became unstable (pressure increased) thus such conditions were avoided. The study presented below were performed under following conditions: MTS flow rate was about 0.012 g/min; current density of 100 mA (maximum power - 200 W) and a total pressure of 7.3 kPa. The N\(_2\):H\(_2\) pressure ratio was 10:1, 4:1 or 3:2. The actinometer was added as previously.

In order to get an information on plasma processes we have studied the evolutions of spectral intensities as a function of experimental time. A series of scans over the emission peaks characteristic of the species of interest (and actinometer) were taken after obtaining the steady-state discharge conditions. It was about 5 minutes after introduction of vapour of MTS to the N\(_2\)-H\(_2\) plasma.
In this analysis the actinometer trends (Ar I, 750.4 nm) have been assumed to be representative of the plasma activity trends [8]. Thus, if the Ar I emission decreases, either the electron density or the mean electron energy (T_e) decreases (or both decrease).

It was found the Ar I intensity fell after introduction of MTS to the plasma. This indicates that the addition of MTS, a polyatomic collision partner, provides efficient relaxation of the high energy electrons implying a reduction in the plasma activity.

One interesting finding was that the spectra intensities of all detected species, with exception of hydrogen, in spite of different variations with time, increased with the nitrogen fraction in the feed. This must be due to increase in the electron density, as it was found for the N_2:H_2 plasma, and indicate on reactions by electron collision as dominant excitation and dissociation mechanisms in the plasma.

![Fig. 3](image)

Fig. 3. Relative intensities of Si I, Ar I, CN, CH and normalized intensities of H_2 and N_2 as well as the intensity ratio I(N_2)/I(N_2) vs time for the mixtures of (a) N_2:H_2=10:1 and (b) N_2:H_2=3:2.

The N_2 band head (380.4 nm) intensity have followed very similar behaviour with time to the Ar I intensity changes (not shown). We interpret this as indication of validity of the actinometric technique for N_2 in the MTS-N_2:H_2 plasma. In the case of hydrogen, although the normalized intensities have been followed, these can not be considered directly representative of concentration trends since different sources for the excited H-atoms can exist in the plasma. The excitation conditions of Si, CH and CN probably also do not fulfil the preconditions for actinometry. Therefore, for this species the relative emission intensity values are presented here. In Figs.3a and 3b, are collected the normalized intensities of N_2 (380.4 nm) and H_2 as well as the relative intensities of Si I (288.1 nm), Ar I (750.4 nm), CH (431.4 nm) and CN (388.4 nm) vs time for the plasmas with the highest and the lowest amount of nitrogen in the feed, respectively. We have also included changes in the intensity ratio of I(N_2)/I(N_2) for the initial conditions.

As can be seen, the Si I intensity fell very rapidly to around of 20% of its initial value within about 5 minutes and then decreased continuously. After about 20 min, the Si I intensity did not change appreciably with time, but there was hardly measurable. This behaviour can be result of recombination of silicon precursors (SiCl) with other plasma species and/or an decreasing fragmentation of the MTS molecules by electron impact due to markedly decrease in the plasma activity (especially at the beginning) or simply can be connected to some extent with an decrease in the supply of MTS to the plasma (unfortunately, this factor can not be excluded). Another a very probable explanation for the Si I changes is that a major factor responsible for the production of atomic Si in the plasma is plasma etching or sputtering which efficiencies depend strongly on the plasma composition and deposition time.
The relative intensities of CH and CN have also decreased continuously with time, but at a lower extent than Si I decreased (Figs.3a,b). The main CH precursor is probably the methyl radical CH₃ which may readily be produced by fragmentation of the MTS molecules by free plasma electrons. Electron impact dissociation of CH₃ radicals can be the main route for the formation of excited CH and the CH radicals in their ground state. The steep decline in the CH intensity may be considered the result of different factors, namely

(a) an decrease in MTS decomposition efficiency and/or in dissociative excitation of CH₃ due to drop in the plasma activity,

(b) further interactions of CH₃ derived species with N₂ and H₂ resulting in more stable carbon-containing species that cannot be identified by OES

(c) an decrease in the supply of MTS to the reactor.

CN radical arises from the reaction of nitrogen species with carbon-containing species in the plasma. A number of pathways leading to its appearance has been reported [9]. Because of the abundance of N₂ in the plasma, CN concentration is expected to be limited by concentration of carbon-containing species what is consistent with our observation. In Fig.4 are shown the intensity ratios of I₁₈/N₁₁ vs time, for the three studied plasmas.

Fig.4. The I₁₈/N₁₁ intensity ratio vs time.

The ratio seems to remain relatively constant with time, but the mean value of I₁₈/N₁₁ for the mixture with N₂:H₂=3:2 was markedly the lowest.
The comparison of the time dependence of I₁₈/N₁₁ ratio for different composition of the diluent gases is presented in Fig.5. As this figure reveals, the ratio rapidly decreased at the beginning and then keep almost constant. The I₁₈/N₁₁ values increased with the N₂ fraction in the feed.

Referring back to Figs.3a,b, in the N₂-based plasma, the N₂ concentration decreased only slightly initially (~20%) then increased and after about 20 min remained fairly constant on a relatively high level. In the case of plasma with much lower amount of N₂ in the feed (N₂:H₂=3:2), the N₂ concentration fell with time and after about 15 min was reduced to about 50% of its initial value. After this decay, a slow increase with time in the N₂ concentration was observed. The above results shown that nitrogen was consumed by plasma reaction, mainly by reaction leading to CN formation. As in the N₂-based plasma the supply of N₂ was very large, the decay in the N₂ concentration has only been observed under conditions of high concentration of carbon-containing species (at the beginning of the process).

It is also interesting that the emission intensities ratio I(N₂)/I(N₂) was changed vs time in the quite opposite way to the N₂ concentration changes (see Figs.3a,b). In our opinion, the observed rise of the intensity ratio indicates on multi-step excitation of N₂ and an increase of the electron density.

A feature of actinometric concentration of hydrogen atoms was that while the plasma activity decreased (at the beginning of the process), the values of I₃/I₈ decreased only slightly with time (N₂:H₂=10:1, Fig.3a) or increased and showed a maximum at about 10 min (N₂:H₂=3:2, Fig.3b). As it
was pointed out earlier, the evolution of normalized intensities of I_h/I_M can not be considered directly representative of the atomic hydrogen concentration trends since many possible sources for the excited H atoms exist in the plasma. In particular, cracking of carbon-containing radicals (i.e., CH_4 + e→CH_3 + H^+ + e) cannot be neglected. Nevertheless, the described above behavior of the normalized intensity seems to be result of chemical reactions involving silicon-containing species (i.e., SiCl+H_2→SiCl-H+HCl) which are the additional source of atomic hydrogen.

Acknowledgments

The authors thank the Centre of Advanced Materials and Nanotechnology Wroclaw University of Technology for financial support.

References