IN SITU CHARACTERIZATION OF PLASMA-MOCVD OF TI-C-N FILMS

S. Peter, F. Richter

Technische Universität Chemnitz-Zwickau, Institut für Physik, D-09107 Chemnitz

Abstract

A plasma-MOCVD process using the precursor tetrakis(diethylamido)titanium (TDEAT, $Ti(N(C_2H_5)_4)$) was investigated by means of *in situ* methods. The particle flux towards the growing layer was studied using a two-stage differentially pumped quadrupole mass spectrometer equipped with an energy analyzer and optical emission spectroscopy. A reduction of excess free carbon in the Ti-C-N layers deposited at 150 °C can be *in situ* monitored by measuring the amount of energetic $C_xH_y^+$ in the ion flux towards the growing film as well as by the intensity of the plasma induced optical emission of the CH radical at 431.4 nm.

1. Introduction

Low-temperature plasma CVD using organometallic titanium precursors was studied during the last years with regard to application in semiconductor technology [1] as well as for tribological purposes [2]. The reduction of excess carbon in the films is one of the major problems during low temperature plasma MOCVD of Ti-C-N [3]. The reaction mechanism involved in plasma enhanced CVD has not been well understood yet, due to the complexity of the reaction system [4]. The molecular and atomic species of the gas phase are excited, ionized or dissociated. Under the conditions of plasma controlled layer formation (negligible thermal decomposition) the spectra of ions extracted at the substrate plane are more representative for the film formation process than the thermal neutrals. The sticking probability for energetic ions and neutrals from low-frequency pulsed discharges is expected to be large. Modelling the stoichiometry of plasma-deposited C:H- films it was shown [5] that sputtering and reflection of ions may be neglected for ions with energies of about 100 eV, which is in the same range of energies as measured in our experiments [6].

2. Experimental investigations

A PACVD apparatus with a parallel-plate arrangement (see schematic in fig. 1) was used both for plasma deposition of hard coatings and *in situ* diagnostics of the deposition process. The flows of the liquid precursor TDEAT and the gases H_2, N_2, NH_3 and Ar were controlled by mass flow meters. In the investigations presented here a constant total pressure of 3 mbar measured with a capacitance manometer was con-

trolled by a throttle valve. The temperature of the substrates (polished silicon wafers) was stabilized by an additional resistance heater.

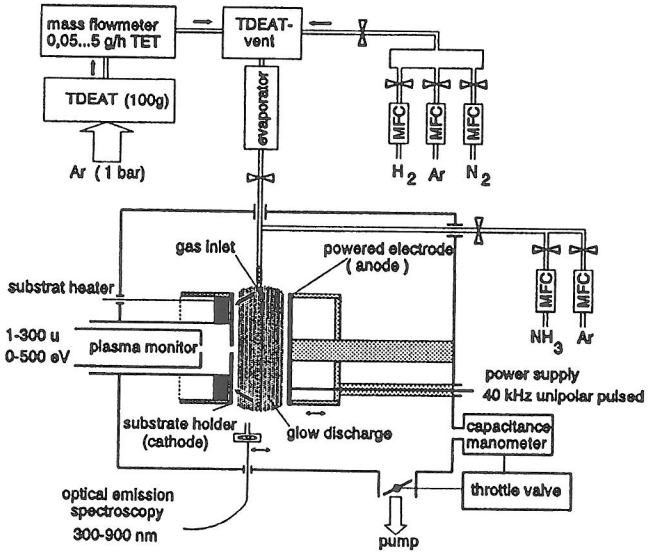

Fig. 1: Plasmachemical deposition system with *in situ* diagnostic equipment

Very low temperature (150°C) was used to deposit films at a growth rate of 10...50 nm/min. Since TDEAT decomposes thermally only at temperatures above 160 °C [7], these depositions are completely under control of the 40 kHz unipolar pulsed plasma excitation. A few comparative deposition experiments were carried out at 400 °C (thermal plus plasma excitation).
Mass spectra and energy distributions of particles striking the cathode were measured using a two-stage differentially pumped plasma monitor (mass range 1...300 u, ion energy range 0...500 eV). The sampling orifice of the plasma monitor was mounted in the centre of the cathode.
Plasma-induced optical emission of numerous excited species (CH, H, NH, Ti, Ar, N_2) has been measured in the wavelength range 300...900 nm.

3. Results and discussion

Deposition from H_2/Ar/TDEAT discharges, i. e. without an additional nitrogen source, results in porous films with high excess carbon concentrations.
First, the addition of nitrogen gas, which is mostly used in Plasma-MOCVD, was investigated. In fig. 2 the influence of the precursor flow rate in H_2/N_2/Ar/TDEAT discharges on the mass distribution of 100 eV ions is shown.
Without precursor the known types of ions for hydrogen-nitrogen-argon discharges are observed: H_x^+ x=1...3, NH_y^+ y=1...4 ,N_2H^+ and ArH^+ (low intensity only).

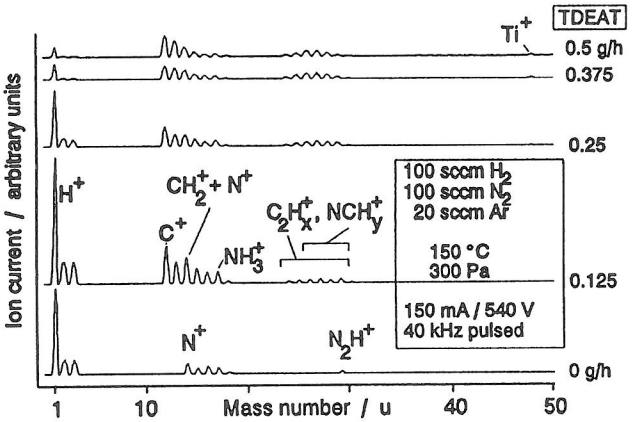

Fig. 2:
Mass spectra of ions extracted from TDEAT/H_2/N_2/Ar discharges in dependence on the precursor flow rate

NH_y^+ ions are formed from the plasmachemically synthesized ammonia. For a stoichiometric H_2+N_2 mixture and similar discharge conditions a steady-state degree of NH_3 synthesis below 1 vol-% was reported in the literature [8]. With increasing precursor flow rate the carbon-containing ions predominate (cf. fig. 2).
The plasma chemistry changes drastically when ammonia is used as the additional nitrogen source. Figure 3 shows the influence of NH_3/H_2 ratio on the mass spectra of ions.

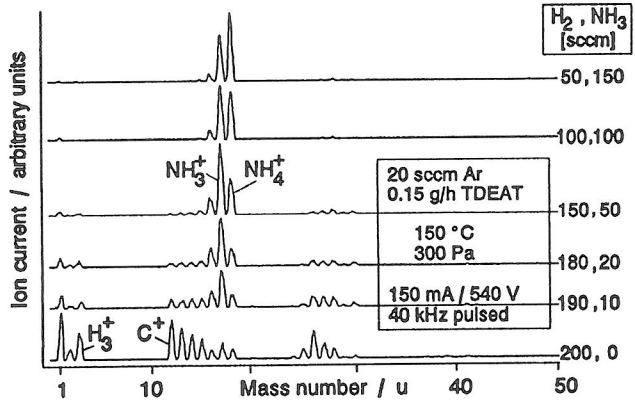

Fig. 3:
Mass spectra of ions from TDEAT/H_2/-NH_3/Ar discharges in dependence on the H_2/NH_3 flow ratio

From the ion mass-scan at the bottom of fig. 3 it is evident, that in H_2/Ar/TDEAT discharges the hydrocarbon ions dominate. An addition of only a few percent of NH_3 to a H_2/Ar/TDEAT discharge results in a drastic reduction in the flux of $C_xH_y^+$ ions

towards the growing film. At ammonia concentrations above 10 % nearly the whole ion current consists of NH_x^+ ions.
The measured portion of carbon-containing ions in the ion flux to the cathode corresponds with the carbon incorporation in the deposited Ti-C-N layers. Films deposited at 150 °C from TDEAT/H_2/N_2/Ar atmospheres are still characterized by a high carbon content. They are polymer-like and sensitive to electron and ion beams during film analysis. Using ammonia gas, the carbon content in the films is reduced and the higher TiN content improves the mechanical properties (not reported here). Results of XPS analysis providing information on predominate bindings are given in fig. 4.

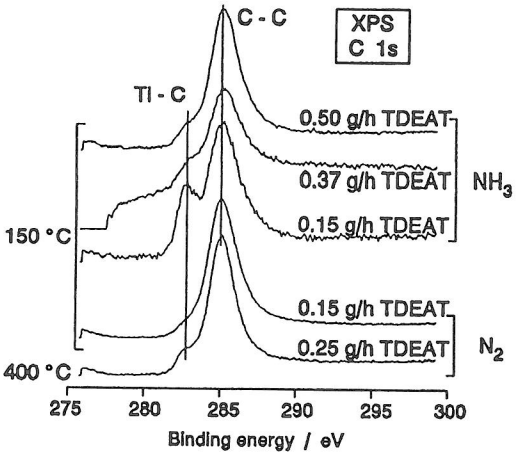

Fig. 4:
X-ray photoelectron spectra (C1s) of Ti-C-N films

The films consist mainly of TiN and free carbon. A certain however small TiC content was found when low TDEAT flow rates and low current densities were used together with ammonia as nitrogen source. Rutherford backscattering (RBS) was used to determine the titanium content of the 2...9 μm thick films (fig 5).

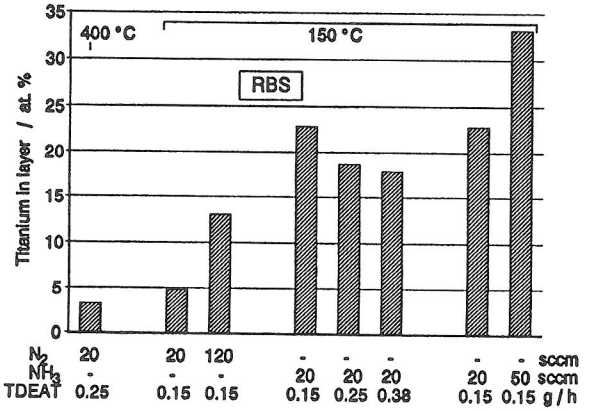

Fig. 5:
Atomic concentration of titanium in Ti-C-N films from RBS measurements

The examples in fig. 5 illustrate, that the titanium content mainly depends on the precursor flow rate and the kind and flow rate of the additional nitrogen carrier. Hydrogen concentrations in the films of 12...23 at-% were measured by elastic recoil detection (ERD).

Another correlation of *in situ* diagnostic results with properties of the deposited films was found for the plasma induced optical emission. The absolute emission intensities of the CH radical at 431.4 nm seems to be proportional to the C/Ti ratio in the layers (fig. 6). The emission was sampled from the negative glow, where near to the cathode a high plasmachemical reaction rate is expected. The intensities, corrected for background, have been measured during very different deposition experiments.

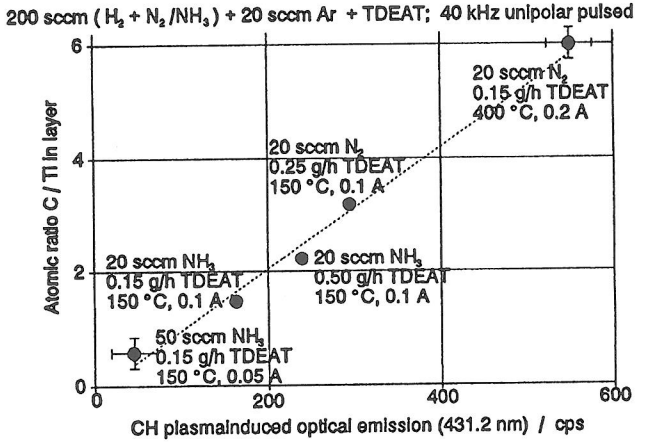

Fig. 6:
Correlation of the plasma induced CH-emission at 431.4 nm with the C/Ti ratio in the Ti-C-N films

One of the measurements was obtained with 400 °C substrate temperature, but due to the high discharge current in this case also plasma controlled deposition dominates. The result in fig. 6 may be explained assuming, that both the CH radical emission and the C/Ti ratio in the films are proportional to the gas phase concentration of small hydrocarbons like CH near the substrate surface (cathode):

- The main volatile reaction products of the precursor formed in the glow discharge are stable amines [9]. We assume that the deposited carbon is a result of film growth from small fragments like the CH radical.
- The measured $A^2\Delta$-$X^2\Pi$ (0,0) band of CH is a transition to both electronical and vibrational ground state [10] with a low excitation energy of 2.9 eV. A direct linear relation between the optical CH emission intensity and the CH gas phase concentration was found during comparative OES and LIF measurements on CH_4 plasmas [11].
- The precursor contains much more carbon than titanium (Ti:C = 16:1). The atomic ratio $[C/Ti]_{layer}$ of carbon to titanium in the films may be written as:

$$[C/Ti]_{layer} = \frac{16 * [TDEAT]_{input} * X_C}{1 * [TDEAT]_{input} * X_{Ti}}$$

$[TDEAT]_{input}$...TDEAT flow rate
X_C, X_{Ti} .... fraction of deposited C and Ti resp.

Under our experimental conditions (sufficient discharge power, low TDEAT flow rate) nearly all the titanium is deposited ($X_{Ti} \approx 1$). The atomic ratio C/Ti hence is proportional to the fraction of deposited carbon from CH_x radicals.
This correlation of the gas phase concentration of hydrocarbon radicals and the film stoichiometery also applies to the interpretation of the ion mass spectra: Ions are formed by electron impact ionization from just these radicals. Therefore, the flux of the respective ions to the substrate surface hence will also be meaningful for *in situ* monitoring of the carbon concentration in the deposited Ti-C-N films.

4. Conclusions

Under the conditions of low-frequency plasma controlled layer formation and minor thermal deposition, especially the flux of energetic ions considerably contributes to the layer formation. The analysis of the ion component therefore provides substantial information on the film formation process. A reduction of excess free carbon in the Ti-C-N layers deposited at 150 °C using the precursor tetrakis(diethylamido)titanium can be *in situ* monitored by measuring the amount of energetic $C_xH_y^+$ in the ion flux towards the growing film.
The absolute emission intensity of the CH radical at 431.4 nm was found to be proportional to the carbon-to-titanium ratio in the layers.

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