Ti(C,N) films deposited from organometallics using LT PACVD[1]

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Abstract – Study of the PACVD process focused on Ti(C,N) films deposited at low temperatures (100–300 °C) from TDEAT and TDMAT precursors. Five process variants were examined to elucidate the effects of process variables on the chemical composition and cohesion of the films. Films having the highest titanium contents and exhibiting a satisfactory cohesion and adhesion were produced from a TDEAT/TDMAT-hydrogen atmosphere by dc plasma assisted LT CVD.

1. Introduction

The CVD process yielding surface films from chemical vapors has become widespread during the last 25–30 years [1, 2]. For some time now, it has been a matter of prime importance to engage in further process developments aiming to lower the film deposition temperatures while retaining the service properties of the coatings [3, 4]. Films of high microhardness are crucial for engineering applications but CVD coatings are no less important for commercial electronics and other industries.

Eventually, the over-all acceptance of the LT CVD processes (PACVD included) will depend on the advances reached by the development of the different process components involved, in order to bolster the inherently less efficient low-temperature chemical deposition by adopting the optimal precursors and by activating the most effective supporting physical mechanism.

In addition to $TiCl_4$ there are other precursors to TiN, TiCN and TiC thin films by organometallic chemical vapor deposition (OM CVD) potentially suitable for the PACVD process, notably tetrakis(diethylamino)titanium(IV), synonymous with titanium(IV) tetrakis(diethylamide), TDEAT, and tetrakis(dimethylamino)titanium(IV), TDMAT. The first of the two, TDEAT, of the formula $C_{16}H_{40}N_4Ti$, is a liquid at room temperature, with a vapor tension of 50 mTorr at 60°C, which turns to gas at 60–100 °C [5]. TDEAT has a molecular weight of 336.38 and its Ti, N, C, and H contents are 14.24, 16.65, 57.13, and 11.98 %, respectively. Its analog TDMAT, of the formula $C_8H_{24}N_4Ti$ and of 224.17 molecular weight), transforms from liquid to gas at somewhat lower temperatures (ca. 30–50 °C).

The present project aimed at examining various options of the chemical deposition process available for the preparation of thin films from the vapors of these organometallics.

2. Experimental

The Ti(C,N) films having 0.1–3 μm in thickness were prepared by the low temperature, plasma activated CVD process (LT PACVD) on polished tool steel and silicon wafer substrates. The deposition process was conducted in vacuo (at 130–145 Pa pressure) for max 3 hours. The TDEAT and TDMAT precursors (cf. above) were used. The processes or rather, process variants examined (Table I) differed by the deposition chamber atmosphere (used in blends with precursor gas) and also by the type of plasma discharge used – both dc plasma (at current densities of max 3.6 mA/cm^2 and negative bias of max 1000 V) and rf plasma (at 13.56 MHz frequency and max 3.0 W/cm^2 power density) were employed.

Table I. Processes used to deposit Ti(C,N) films

process	precursor	reaction/ carrier gas	plasma	deposition temperature
1	TDEAT	N_2	dc	250–300 °C
2		NH_3		
3		H_2		100–300 °C
4			rf	250–300 °C
5	TDMAT		dc	

Thus there were three processes (positions 1–3 of Table I) using dc plasma, which differed from one another only by the type of gas atmosphere used (nitrogen, ammonia, hydrogen). Additional trials of the #3 process (TDEAT – dc plasma – hydrogen) attempted deposition at (relatively) very low temperatures (100–150°C). In the #4 process, deposition in rf plasma was tested.

The reason why N_2, NH_3, and H_2 atmospheres were chosen was to study the changes in the carbon,

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nitrogen, and titanium contents in the deposits and to establish what relative changes – in particular, what changes in the (C+N)/Ti ratio – corresponded to the different gases used. The #4 process was applied to test the capacity of the other precursor to Ti(C,N) films – tetrakis(dimethylamino)titanium(IV), TDMAT (cf. above).

3. Results

The negative bias required to reach a deposition rate of approx. 1 μm/h with dc plasma was ~400 V for #1 process, ~600 V for #2 process, and ~900–1000 V for #3 process (cf. Table I). Subsequent to deposition, some of the #2 and #3 process specimens were annealed at 550 °C for 2 h in NH_3 or N_2 atmosphere, in order to identify any changes to film composition.

For orientation, additional #3 process tests were run aiming to deposit the films at even lower temperatures, specifically, at 100–150 °C. It has been found that even at such temperatures the precursor will decompose to satisfaction, but the film adhesion suffers.

The #4 process tests were performed using rf plasma (cathode voltage –200 V, input power density 1.5 W/cm^2).

The objective of the #5 process was mainly to determine the carbon concentrations in films obtained from a precursor of different carbon content. Negative bias of 950–1000 V was applied here.

The primary responses studied for these processes were the composition and the adhesion of the films. We wanted to find out more about the carbon, nitrogen, and titanium contents in the films and about the effects on these of the deposition chamber atmosphere.

The GDOES depth profiles determined for #1 process films (TDEAT – dc plasma – nitrogen) showed that the steady-state composition reached at the depth of ca. 0.25–0.50 μm under the surface was, approximately, 15 at.% Ti, 33 at.% C, and 52 at.% N. Reproducibility of the composition was good. Adhesion however, based i.a. on static indentation tests, was mediocre.

The #2 process films (TDEAT – dc plasma – ammonia) contained ca. 17 at.% Ti, 35 at.% C, and 48 at.% N. Reproducibility was inferior to that for #1 process films. Adhesion was impaired by annealing at 550 °C/2 h/NH_3.

The #3 process films (TDEAT – dc plasma – hydrogen) contained ca. 23 at.% Ti, 30 at.% C, and 42 at.% N. Reproducibility was good. The hydrogen content was not determined. Subsequent annealing produced no changes to the Ti/C/N ratios. Thus, these films were enriched in titanium and depleted of nitrogen, in comparison to the films prepared in the presence of either N_2 or NH_3. The films developed cracks during the indentation tests.

The #4 process films (TDEAT – rf plasma – hydrogen) contained less titanium (~21 at.%) and more carbon (~54 at.%) than the films deposited from the same environment in dc plasma. This is in agreement with the findings of authors from Fraunhofer-Institut für Schicht- und Oberflächen-technik at Braunschweig, Germany [6]. The oxygen content in the film was increased, too: whereas the films produced from TDEAT in dc plasma had oxygen contents far below the 1 % level, the films deposited in rf plasma contained up to 10 % oxygen.

The #5 process films (TDMAT – dc plasma – hydrogen) were mostly amorphous but with minute crystals, as evidenced by the peaks in the X-ray diffractogram (Fig. 1). The films contained ca. 29.5 at.% Ti, 48 at.% C, 19 at.% N, and 3 at.% O. Thus they contained more titanium (and also more oxygen) than the corresponding films produced from TDEAT precursor.

A summary of the film composition data is given in Table II. The + or – signs in the H column indicate the likelihood of the presence of hydrogen in the films.

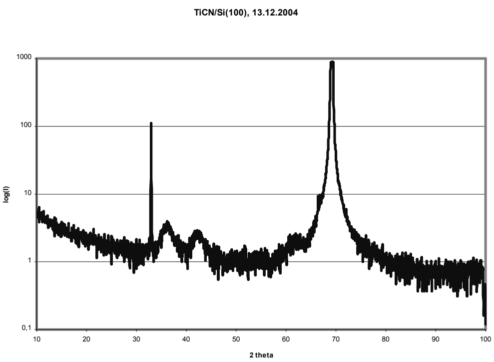

Fig. 1. X-ray diffraction of #5 process Ti(C,N) film

Table II. – Elemental composition of Ti(C,N) films prepared by LT PACVD processes

Element, at.% → Deposition process↓	Ti	C	N	O	H
1 = TDEAT-dc plasma-N_2	15	33	52	–	–
2 = TDEAT-dc plasma-NH_3	17	35	48	–	+
3 = TDEAT-dc plasma-H_2	23	30	42	–	+
4 = TDEAT-rf plasma-H_2	21	54	14	10	+
5 = TDMAT-dc plasma-H_2	29.5	48	19	3	+

4. Conclusion

Titanium carbonitride films were prepared by the LT PACVD process at temperatures no higher than 300°C. Two organometallic precursors were used, *viz., tetrakis(dietylamino)titanium*(IV) (TDEAT) and *tetrakis(dimethylamino)titanium*(IV) TDMAT), coupled with a suitable generic process capable of operating at temperatures below 300 °C, which if brought to perfection would have the potential of producing optimized, quality Ti(C,N) coatings.

The following tentative conclusions can be drawn:

1. The chemical composition of Ti(C,N) films prepared from organometallics is influenced by the type of atmosphere from which the film is deposited onto the substrate.
2. The measurements indicated that coatings having the highest titanium contents and the best composition over-all were produced from atmospheres where the precursor gas was blended with hydrogen.
3. The highest nitrogen contents were found in films deposited from nitrogen or ammonia based atmospheres.
4. Annealing at 550 °C under nitrogen or NH_3 had little effect on the chemical composition of the films (obtained at temperatures below 300 °C).
5. The films had mediocre adhesion to steel substrates, making it imperative to upgrade specimen pretreatment and to meticulously attend to surface pre-cleaning. In view of the low film thicknesses, it is also the hardness measurements which require improved pretreatment and perfectly polished, minimum roughness substrates. Future experiments will focus on producing films of optimum composition and on testing mainly their hardness and adhesion.

References

[1] H.O. Pierson, *Handbook of chemical vapour deposition – principles, technology and application*, Noyes Publications, NJ, USA, 1992, ISBN 0-8155-1300-3, 436 pp.

[2] F. Cerný, D.Tischler, M.A.K. Ibrahim, S. Konvicková, B. Sopko, S. Horejs, J. Fajkus, *High temperature oxidation resistance of CrN_X coatings prepared by electron beam evaporation and IBAD methods*, Poster presentation at AEPSE'2005 (5th Asian-European International Conference on Plasma Surface Engrg), Qingdao, China, 12–16 Sept 2005.

[3] J.M. Lackner, W. Waldhauser, R. Ebner, *Large-area high-rate pulsed laser deposition of smooth TiC_xN_{1-x} coatings at room temperature – mechanical and tribological properties*, Science Direct online, 27.08.2004.

[4] L. Alberts, D. Boscarino, A. Patellic, V. Rigatoc, H. Ahn, K. T. Rie, Surface & Coatings Technology 169–170, 388 (2003)

[5] K.T. Rie, J. Wöhle, Surface & Coatings Technology 112, 226 (1999)

[6] J. Wöhle, A. Gebauer-Teichmann, K.-T. Rie, Surface & Coatings Technology 142, 661 (2001).