ADSORPTION AND THERMAL DECOMPOSITION OF TETRAKIS-(DIMETHYLAMIDO)TITANIUM ON Si AND SiO_2/Si SURFACES: AN XPS STUDY*

Michaela JANOVSKA and Zdenek BASTL

J. Heyrovsky Institute of Physical Chemistry,
Academy of Sciences of the Czech Republic, 182 23 Prague 8, The Czech Republic

Received October 27, 1994
Accepted December 1, 1994

X-Ray photoelectron spectroscopy (XPS) has been used to study adsorption of tetrakis(dimethylamido)titanium (TDMT) on a clean Si surface and surface on which an oxide layer was grown prior to TDMT adsorption. Measurements were carried out at temperatures 80 and 295 K. In addition, decomposition of TDMT on the above substrates yielding titanium nitride coatings was investigated. The change in surface composition as a function of TiN_x layer thickness was monitored by XPS. Adsorption at 80 K proceeds without dissociation on both substrates. Photoelectron spectra measured at 295 K indicate presence of surface species containing C–N multiple bond on both substrates and on SiO_2/Si substrate formation of species that contain Ti–N–C rings. At 580 K an overlayer consisting predominantly of TiN_x was produced by pyrolysis of TDMT. The photoelectron spectra revealed also presence of species with C–N–C, Si–CH_x and Ti–C bonds the concentration of which depended on an overlayer thickness. On SiO_2/Si substrate decomposition of SiO_2 accompanied by titanium oxide formation occurs during initial stages of TDMT pyrolysis.

Tetrakis(dimethylamido)titanium, $Ti[N(CH_3)]_4$, (TDMT) is frequently used as a single-source precursor for metalloorganic chemical vapour deposition (MOCVD) of titanium nitride films[1] which are regarded at present as one of the most important technological coatings. Thin films of titanium nitride are extremely hard and chemically inert. They exhibit exceptional wear and corrosion resistance and have many important applications in microelectronics, as hard coatings for tools, as solar control coatings, sensors or as catalysts. The quality of the TiN films significantly depends on their stoichiometry and is substantially influenced by the presence of impurities. The use of a single-source precursor in the deposition of TiN has many advantages compared to methods using mixtures of two or more precursors. The TiN films can be prepared from TDMT at rather low substrate temperatures (200 – 400 °C) but, unfortunately, they are usually

---

* Presented at the *XXVIth Czech and Slovak Symposium on Catalysis, Prague, November 7 – 8, 1994.*

contaminated by carbon. Significant efforts have been exerted towards elucidation of the mechanisms of chemical reactions occurring during TDMT decomposition[2–5] on solid surfaces but unambiguous explanation is still missing.

An important step in the growth of films is the nucleation process which in the case of compound as TiN is rather complex and obviously involves a series of chemical reactions. On inert substrates no chemical reactions occur between precursor and the substrate. Precursor molecules are adsorbed on the substrate surface and react there. The extent and mode of adsorption depend on the pressure, temperature, substrate material, its crystallographic orientation and on the concentration of surface defects. Consequently, the nucleation behaviour may be different on different substrate materials. On reactive substrates an overlayer consisting of adsorbed and partially reacted molecules is formed and nucleation becomes more complex than on inert substrates.

In the present study X-ray photoelectron spectroscopy (XPS) was employed to investigate adsorption of TDMT on clean Si surface and on the surface on which an oxide layer with thickness ≈0.5 nm was grown prior to adsorption. The measurements were carried out at liquid nitrogen temperature and at room temperature. In addition, the products of decomposition of TDMT at 580 K on these substrates were also studied.

EXPERIMENTAL

The adsorption experiments were carried out in preparation chamber (base pressure $6 . 10^{-8}$ Pa) of a VG ESCA 3 Mk II electron spectrometer. The Si substrate temperature could be varied in the range 80 – 1 000 K and was measured by a thermocouple attached to the sample. The Si (100) wafers were first cleaned by Ar ion sputtering (4 kV, 10 μA/cm^2, 30 min). The oxide layers 0.5 ± 0.1 nm thick were grown at 970 K by exposing clean Si surface to $6.7 . 10^{-3}$ Pa of molecular oxygen for 20 min. The cleanliness of Si and SiO_2/Si surfaces was checked by XPS method prior to TDMT adsorption. TDMT (99.8%) was purchased from Schumacher (Germany) and was used without further purification. The samples were transferred to the spectrometer analyzer chamber (base pressure better than $5 . 10^{-8}$ Pa) under UHV conditions. XPS measurements were made using AlKα radiation ($h\nu$ = 1 486.6 eV) from an Al/Mg twin anode run at 230 W. The 150° spherical sector analyzer was operated in the fixed analyzer transmission mode (FAT) at a pass energy 50 eV for survey spectra and 20 eV for high-resolution spectra. The angle between the sample surface and direction of photoelectron collection was 25°. Spectra of Ti 2*p*, N 1*s*, C 1*s* and O 1*s* photoelectrons were recorded. Peak area computation was performed after the non-linear background[6] was removed. The atomic concentration ratios and thicknesses of overlayers (expressed in number of effective monolayers; 1 monolayer = 0. 215 nm) were calculated using methods described in literature[7]. Subshell photoionisation cross-sections published by Scofield[8] and electron mean free paths values suggested by Seah and Dench[9] were used in calculations. The overlapping spectral features were resolved into individual components with mixed Lorentzian–Gaussian peak shapes by using a modified version of the non-linear least-squares procedure published by Hughes and Sexton[10].

Photoelectron binding energies were determined relative to Au $4f_{7/2}$ binding energy set at 84.0 eV with an accuracy of ±0.25 eV.

RESULTS AND DISCUSSION

Adsorption of TDMT at 80 K

The Ti 2*p*, N 1*s* and C 1*s* spectra recorded after exposure of clean Si and SiO_2/Si to TDMT vapour at 80 K for 10 min are shown in Figs 1 and 2, respectively. The spectra show no evidence of TDMT decomposition at this temperature. The core level binding energies, peak widths (FWHM) and calculated atomic compositions are summarized in Table I in which also the results obtained after heating the Si sample with adsorbed TDMT at room temperature for 12 h are also displayed. The spectra obtained at 80 K correspond to condensed layer of TDMT and as expected their shape and position do

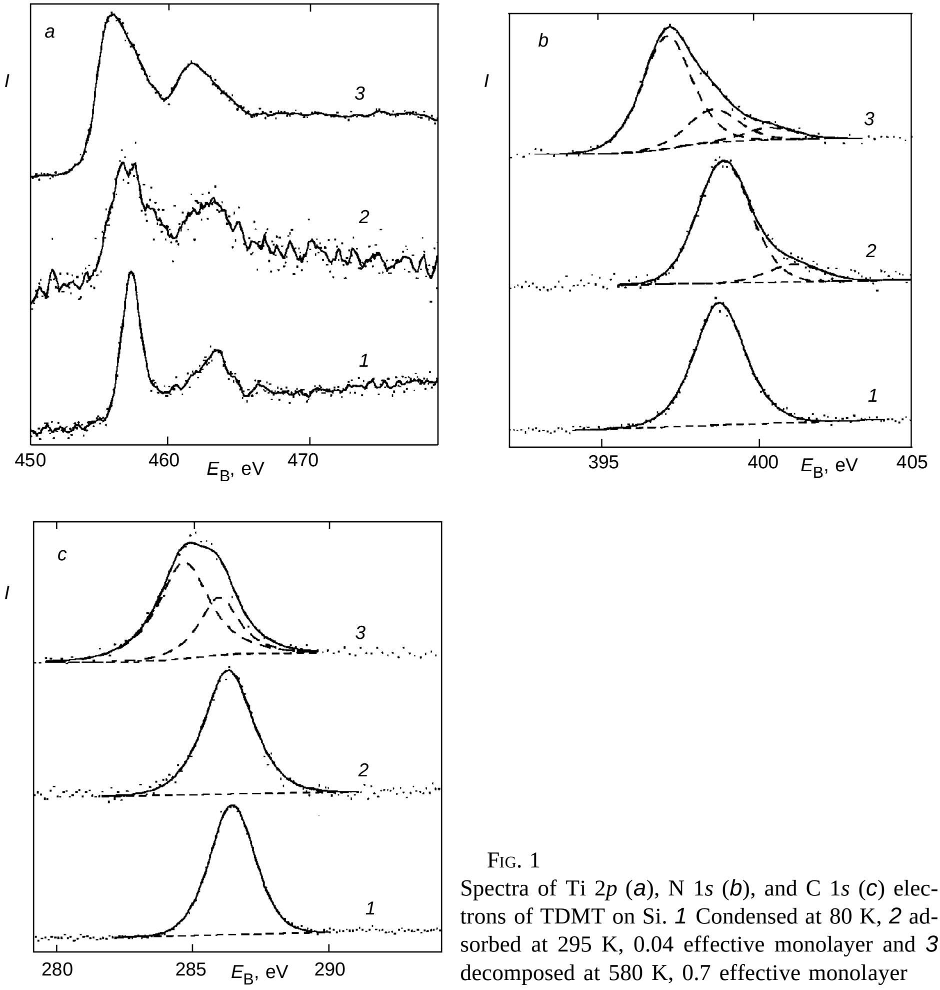

FIG. 1
Spectra of Ti 2*p* (*a*), N 1*s* (*b*), and C 1*s* (*c*) electrons of TDMT on Si. *1* Condensed at 80 K, *2* adsorbed at 295 K, 0.04 effective monolayer and *3* decomposed at 580 K, 0.7 effective monolayer

not depend on whether Si or SiO_2 substrate is used. The substrate photoemission lines were not seen in survey spectra of some samples which indicates that the thicknesses of adsorbed layers were higher than ≈10 nm. Surface static charging was observed and method[7] employing in situ deposition of copper on the surface of condensed layer was used for spectra calibration (binding energy of Cu $2p_{3/2}$ equal to 932.8 eV was employed).

Heating of the sample to 295 K for 12 h leads to the desorption of most of the TDMT adsorbed and to substantial increase of oxygen surface concentration. This oxygen comes from residual gases and, as evidenced from broadening of Ti $2p_{3/2}$ line, is most likely bound to Ti.

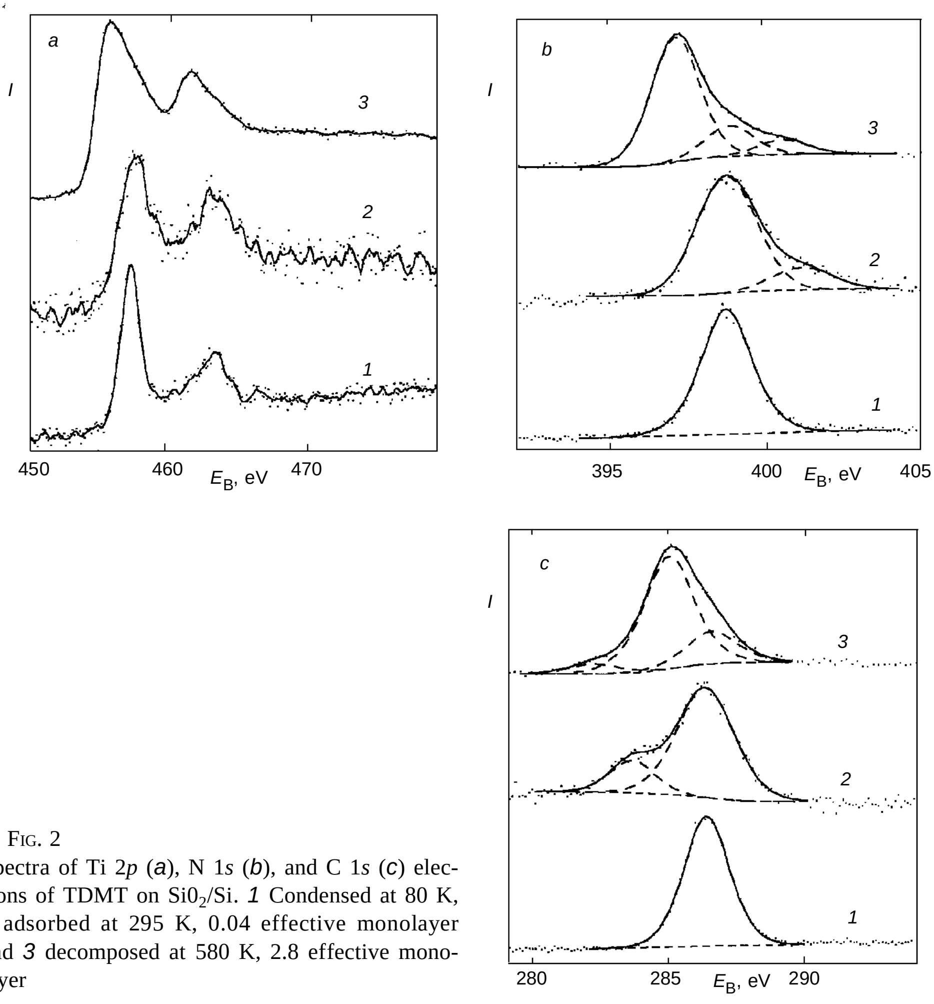

FIG. 2
Spectra of Ti 2*p* (*a*), N 1*s* (*b*), and C 1*s* (*c*) electrons of TDMT on $Si0_2$/Si. *1* Condensed at 80 K, *2* adsorbed at 295 K, 0.04 effective monolayer and *3* decomposed at 580 K, 2.8 effective monolayer

The difference between composition of the condensed TDMT and that expected on the basis of molecular stoichiometry was found (Table I). This difference may be due to the presence of impurities in the condensed phase and/or due to the method used to convert the XPS data to atomic concentrations.

Much work has been undertaken to find reliable and accurate method for TiN_x quantitative analysis. Many techniques, including AES, EDAX, RBS and XPS were applied for this purpose but each of them had problems in quantifying TiN_x composition[11–16]. In XPS the main problems are caused by variable background and a complex intrinsic satellite structure in the Ti 2*p* spectral region, which depends on the sample composition. In calculating the compositions shown in Table I the upper boundary for the background subtraction was set at 466 eV, i.e. in the region of satellites which may cause too low intensity of the Ti 2*p* line. Better results from the point of their agreement with nominal stoichiometry of TDMT were obtained if the end of the spectral region that is to be background subtracted was fixed at 486 eV. Different background subtraction methods were applied in an effort to unravel this problem but difficulties in accurate determination of N/Ti atom ratios were not completely solved. Because of the complicated shape of the Ti 2*p* line we have not attempted throughout this work to decompose it into individual contributions.

Presence of small amounts of oxygen in adsorbed layers probably results from traces of water in background gases.

Adsorption of TDMT at 295 K

Comparable amounts of TDMT were adsorbed at room temperature on Si and SiO_2/Si surfaces. Corresponding photoelectron spectra are shown in Figs 1 and 2. Core level

TABLE I

Core level binding energies, E_B, full widths at half maxima of photoemission lines, FWHM (eV), and atomic composition of layer of TDMT condensed at 80 K on Si ($d \geq 10$ monolayers) and after heating the sample 12 h at 295 K ($d = 0.3$ monolayer; 1 monolayer = 0.215 nm)

Core level	Condensed layer			After 12 h at 295 K		
	E_B	FWHM	composition	E_B	FWHM	composition
Ti $2p_{3/2}$	457.2	1.7	0.2	458.3	2.5	0.3
N 1*s*	398.7	1.8	1.0	399.1	1.6	1.0
C 1*s*	286.3	1.9	2.3	286.5	1.7	2.5
O 1*s*	530.5	2.2	<0.03	531.5	1.8	0.3
	532.5	2.2	<0.02	–		–

binding energies, peak widths and calculated compositions of adsorbed layers are summarized in Table II. Note that the results obtained for TDMT adsorbed on Si at 295 K are not identical to the results obtained after heating Si with TDMT condensed at 80 K to 295 K. The results indicate that a fraction of adsorbed molecules partially dissociates at 295 K. With both substrates the N 1*s* spectra are composed of two peaks, located at 398.8 and 401.2 eV. The second, less intensive peak may be assigned[17] to species that contain C–N multiple bonds. On SiO_2/Si surfaces additional C 1*s* line centered at 283.6 eV is observed (Fig. 2*c*) which may be attributed to carbon atoms present in surface species that contain three-membered Ti-N-C rings. Such complexes can be produced on specific surface active sites by loss of dimethylamine from TDMT and their existence as reaction intermediates in TDMT pyrolysis at temperatures above 400 K was suggested in the literature[5] on basis of infrared spectroscopic studies.

Decomposition of TDMT at 580 K

When Si or SiO_2/Si substrates are heated in ≈0.1 Pa of TDMT their surfaces become covered with a layer containing predominantly titanium nitride with N 1*s* binding energy of ≈397 eV (Table III and Figs 1*b* and 2*b*). The value of Ti $2p_{3/2}$ binding energy also agrees well with values reported in the literature for Ti nitride[14–17]. Additional two peaks of nitrogen can be seen in the N 1*s* spectra. The concentration of nitrogen with N 1*s* binding energy of 398.6 eV decreases with increase of the layer thickness. Simultaneously the concentration of the carbon component with C 1*s* binding energy of ≈286 eV

TABLE II
Core level binding energies, E_B, peak widths, FWHM (eV), and atomic compositions of TDMT adsorbed on Si and SiO_2/Si substrates at 295 K (ML monolayer)

Core level	0.04 ML on Si			0.03 ML on SiO_2/Si		
	E_B	FWHM	composition	E_B	FWHM	composition
Ti $2p_{3/2}$	456.9	3.1	0.13	457.5	2.9	0.15
N 1*s*	398.9	2.0	0.87	398.7	2.3	0.80
	401.1	2.0	0.13	401.2	2.3	0.17
C 1*s*	–		–	283.6	1.9	0.43
	286.2	2.1	2.18	286.3	2.5	1.87
O 1*s*	531.8	2.3	0.10	532.7	2.3	16.87
Si 2*p*	99.7	1.8	–	99.6	1.8	–
	–		–	103.4	2.5	–

decreases (see Figs 3, 4 and Tables III, IV). On the basis of this behaviour we can assign the peaks at 398.6 and 285.9 eV to the compound with C–N–C bonding. The N 1*s* peak at 400.5 eV may be tentatively assigned to oxynitride species but it may be also satellite of the main N 1*s* peak.

The carbon 1*s* peak centered at 284.5 eV is characteristic of hydrocarbons and/or elementary carbon[17]. The binding energy of the third carbon peak, 282.4 eV, present at surface coverage higher than 1 monolayer is typical of metallic carbides[17].

Small amounts of oxygen were found to be always present in the layers. As already mentioned it comes from the reaction of overlayer with residual gases of the vacuum system during photoelectron spectra accumulation. The O 1*s* line can be fitted by two components. The lower binding energy component belongs to titanium oxides, TiO_x, while the higher binding energy peak likely comes from oxygen involved in C–N–O bonding.

TABLE III
Core level binding energies, E_B, peak widths, FWHM (eV), and atomic compositions of surface coatings produced by decomposition of TDMT on Si at 580 K. The thicknesses of coatings are expressed in number of effective monolayers (monolayer = 0.215 nm)

Core level	E_B	FWHM	Number of layers			
			0.2	0.7	1.3	1.9
Ti $2p_{3/2}$	455.6	3.7	0.56	0.97	1.04	0.98
N 1*s*	397.6	1.8	0.52	0.71	0.76	0.69
	398.6	1.8	0.40	0.21	0.16	0.19
	400.5	1.8	0.08	0.08	0.08	0.12
C 1*s*	282.4	2.0	–	–	0.12	0.04
	284.5	2.0	0.67	1.12	1.01	1.07
	285.9	2.0	1.47	0.52	0.34	0.27
O 1*s*	530.2	2.1	0.02	0.15	0.11	0.15
	531.6	2.1	0.43	0.11	0.14	0.03
Si 2*p*	99.5	1.4	10.60	5.15	2.55	1.5
	100.8	1.4	0.69	–	0.19	0.15
Cl 2*p*[a]	199.0	2.7	–	–	–	0.19

[a] Chlorine is present in trace amounts in TDMT.

The Si 2*p* line is clearly composed of two contributions. The main peak at 99.5 eV, the intensity of which decreases with increasing layer thickness belongs to silicon from the substrate. The binding energy of the second peak, 100.8 eV, is consistent with Si–CH_x bonding[17].

On SiO_2/Si substrate partial decomposition of silicon oxide occurs during initial stages of TDMT decomposition. This is clearly evident in the shape and width of Ti 2*p* spectrum (see Fig. 4, spectrum *1*) and correspondingly high intensity of O 1*s* component at 530.3 eV, associated with the oxygen bound to Ti (Table IV).

The results obtained show that both substrates behave at 580 K as reactive. Note that the chemical reaction at interface is a prerequisite of good adhesion of the coating to

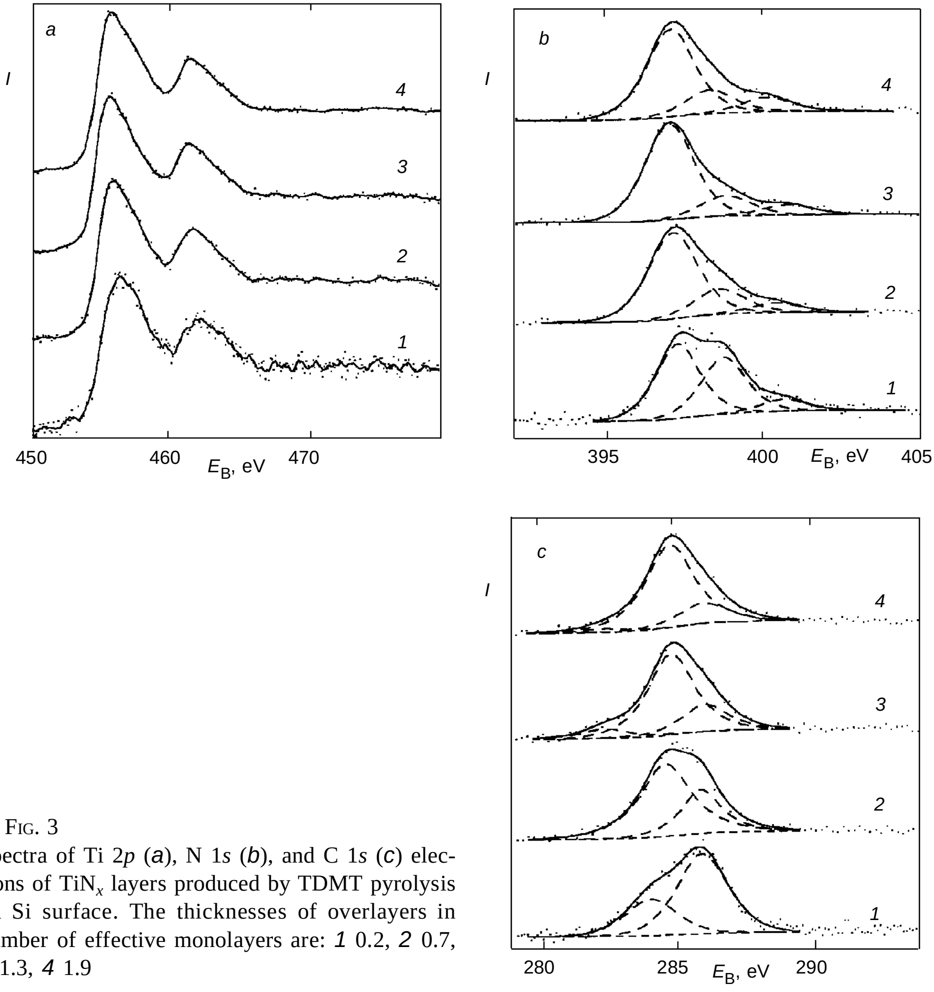

FIG. 3
Spectra of Ti 2*p* (*a*), N 1*s* (*b*), and C 1*s* (*c*) electrons of TiN_x layers produced by TDMT pyrolysis on Si surface. The thicknesses of overlayers in number of effective monolayers are: *1* 0.2, *2* 0.7, *3* 1.3, *4* 1.9

the substrate. This reaction is also responsible for increased concentration of contaminating species at overlayer/substrate interface. It follows from our results that concentrations of carbon present in the coatings as hydrocarbons and/or carbon element are rather high, comparable to concentration of nitrogen, and they do not depend on whether Si or SiO_2/Si substrate is used. Our preliminary angle resolved XPS measurements show that contaminating carbon is not homogeneously distributed within the layer; in addition to interface region an increase at the coating surface was also observed.

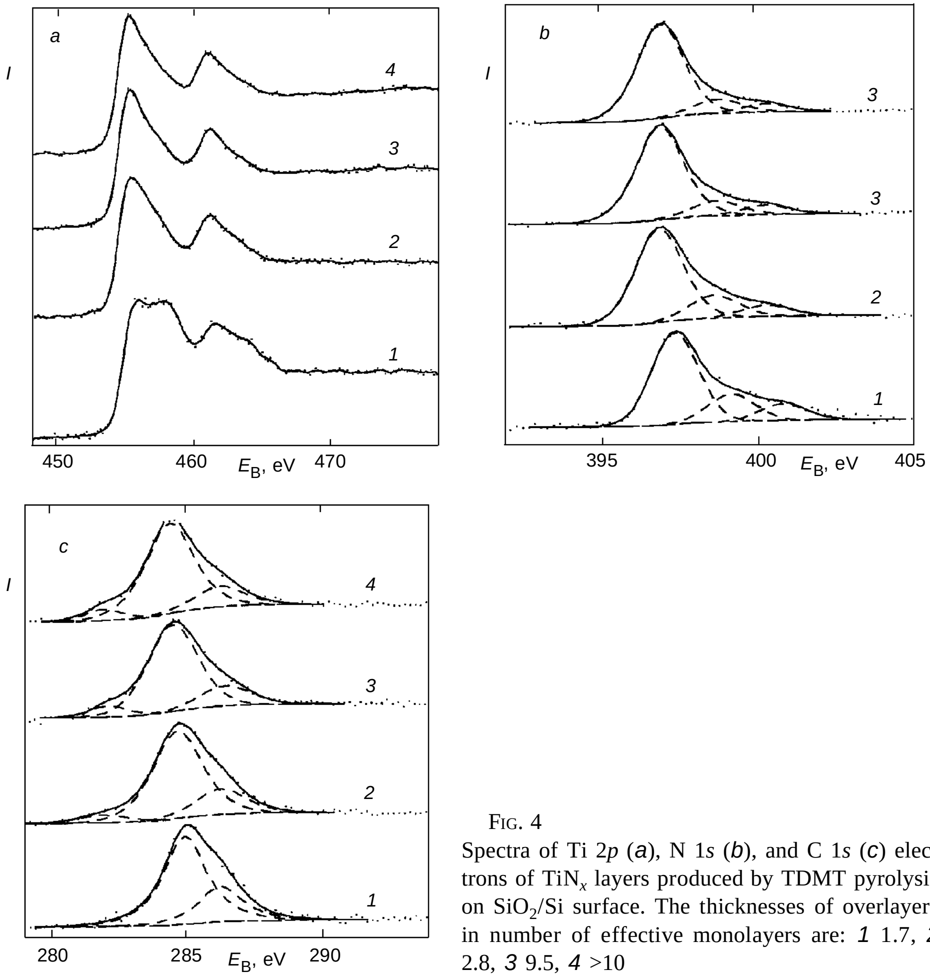

FIG. 4

Spectra of Ti 2*p* (*a*), N 1*s* (*b*), and C 1*s* (*c*) electrons of TiN_x layers produced by TDMT pyrolysis on SiO_2/Si surface. The thicknesses of overlayers in number of effective monolayers are: *1* 1.7, *2* 2.8, *3* 9.5, *4* >10

TABLE IV
Core level binding energies, E_B, peak widths, FWHM (eV), and atomic compositions of surface coatings produced by decomposition of TDMT on SiO_2/Si substrate at 580 K. The thicknesses of coatings are expressed in number of effective monolayers (1 ML = 0.215 nm)

Core level	E_B	FWHM	Number of layers			
			1.7	2.8	9.5	bulk
Ti $2p_{3/2}$	455.4	3.2	1.4	1.2	0.95	1.07
N 1*s*	396.9	1.8	0.67	0.73	0.79	0.81
	398.7	1.8	0.20	0.18	0.13	0.12
	400.3	1.8	0.12	0.09	0.08	0.07
C 1*s*	282.1	1.4	0.01	0.09	0.09	0.11
	284.6	2.0	1.17	1.04	0.97	1.12
	286.2	2.0	0.47	0.30	0.23	0.26
O 1*s*	530.3	2.4	0.74	0.22	0.14	0.13
	532.7	2.0	1.42	0.56	0.07	0.01
Si 2*p*	99.7	1.4	2.22	1.07	0.13	–
	103.4	2.3	0.60	0.31	0.04	–

CONCLUSIONS

Using X-ray photoelectron spectroscopy we have studied chemical composition of layers produced by adsorption of TDMT on Si and SiO_2/Si substrates at 80 and 295 K. Surface species containing C–N multiple bond were identified on both substrates at 295 K. On SiO_2/Si substrate photoelectron spectra indicate presence of species that contain compound with Ti-N-C ring.

We have determined composition of overlayers produced by TMDT pyrolysis at 580 K. Besides titanium nitride the photoelectron spectra have revealed presence of species with C–N–C, C–C, Si–CH_x, Ti–C and Ti–O bonds.

We are currently investigating the mechanisms of carbon incorporation into titanium nitride layers produced by heterogeneous pyrolysis of TDMT.

The support of this work by the Grant Agency of the Czech Republic (Grant No. 203/93/0245) is gratefully acknowledged.

REFERENCES

1. Knizova M.: Chem. Listy *88,* 501 (1994).
2. Sugiyama K., Pac S., Takahashi Y., Motojima S.: J. Electrochem. Soc. *122,* 1545 (1975).
3. Fix R. M., Gordon R. G., Hoffman D. M.: Chem. Mater. *2*, 235 (1990).
4. Katz A., Feingold A., Pearton S. J., Nakahara S., Ellington M. E., Chakrabarti U. K., Geva M., Lane E.: J. Appl. Phys. *70*, 3666 (1991).
5. Dubois L. H., Zegarski B. R., Girolami G. S.: J. Electrochem. Soc. *139*, 3603 (1992).
6. Shirley D. A.: Phys. Rev., B *5*, 4709 (1972).
7. Briggs J. D., Seah M. P.: *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*. Wiley, Chichester 1983.
8. Scofield J. H.: J. Electron Spectrosc. Relat. Phenom. *8*, 129 (1976).
9. Seah M. P., Dench W.: Surf. Interface Anal. *1*, 2 (1979).
10. Hughes A. E., Sexton B. A.: J. Electron Spectrosc. Relat. Phenom. *46*, 31 (1988).
11. Hofmann S.: J. Vac. Sci. Technol., A *4*, 2789 (1986).
12. Perry A. J., Strandberg C., Sproul W. D., Hofmann S., Ernsberger C., Nickerson J., Chollet L.: Thin Solid Films *153*, 169 (1987).
13. Dawson P. T., Tzatzov K. K.: Surf. Sci. *149*, 105 (1985).
14. Robinson K. S., Sherwood P. A. M.: Surf. Interface Anal. *6*, 261 (1984).
15. Vasile M. J., Emerson A. B., Baiocchi F. A.: J. Vac. Sci. Technol., A *8*, 99 (1990).
16. Heide N., Siemensmeyer B., Schultze J. W.: Surf. Interface Anal. *19*, 423 (1992).
17. *NIST X-Ray Photoelectron Spectroscopy Database*. U.S. Dept. of Commerce, Gaithersburg, MD 1989.