Journal of Alloys and Compounds 509 (2011) 6090–6095

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Metalorganic chemical vapor deposition of Ti–O–C–N thin films using TBOT as a promising precursor

O.A. Fouad[a,*], R.A. Geioushy[a], S.M. El-Sheikh[a], M.H. Khedr[b], I.A. Ibrahim[a]

[a] Central Metallurgical Research and Development Institute (CMRDI), P.O. Box 87, Helwan 11421, Helwan, Egypt
[b] Chemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt

ARTICLE INFO

Article history:
Received 30 September 2010
Received in revised form 4 March 2011
Accepted 6 March 2011
Available online 11 March 2011

Keywords:
Ti–O–C–N thin films
MOCVD
XRD
SEM
XPS

ABSTRACT

Ti–O, Ti–O–C and Ti–O–C–N thin films have been synthesized successfully via metalorganic chemical vapor deposition (MOCVD) technique. Tetrabutyl orthotitanate (TBOT) is used as a precursor in presence of Ar, H_2, and N_2 as process gases. By controlling deposition temperature and type of process gases, it was possible to control the composition of the deposited films. The deposited films are composed mainly of Ti and O when H_2 is used as a process gas in the temperature range 350–500 °C. As the temperature increased up to 600 °C, thin films containing anatase (TiO_2) and titanium carbide (TiC) phases are deposited and confirmed by XRD and EDX analyses. As the temperature increased to 750 °C, a transformation from anatase to rutile phase (TiO_2) is started and clearly observed from XRD patterns. Titanium nitride (Ti_2N and TiN) phase in addition to TiO_2 and TiC phases are formed at 600–1000 °C in presence of nitrogen as a process gas. SEM images for all investigated film samples showed that the films are deposited mainly in the form of spherical particles ranged from few nano- to micrometer in size with some additional special features regardless the type of the process gas. Films containing carbon and nitrogen show higher hardness than that containing only oxygen. The obtained results may help in better understanding and controlling film composition and its phase formation in Ti–O–C–N system by MOCVD technique.

1. Introduction

The interest in titanium dioxide (TiO_2) thin films growing has been increased recently because of its technological applications. TiO_2 films can be used as anticorrosive protection, as catalyst in chemical industry and environmental applications. Furthermore, considering its high dielectric constant, this metal oxide has been considered as candidate to replace SiO_2 in the metal-oxide semiconductor (MOS) gates in the microelectronic industry [1]. On the other hand, titanium carbide (TiC) is a typical transition metal carbide and is one of the frequently used protective thin film materials [2]. It has a NaCl crystal structure, with high melting point (3100 °C), high hardness, good thermal conductivity and high thermal shock resistance [3]. It can be used in microelectronic industry as a diffusion barriers and optical filters. Moreover, titanium nitride (TiN) films are widely used in a number of important industrial applications. Major uses of TiN films include cutting and grinding tools, wear surfaces, decorative and semiconductors [4]. Also, TiN is extensively used as diffusion barriers in integrated circuits (ICs) technology due to its high thermal stability and low electrical resistivity (several 10 μΩ cm) [5].

Ti(C,N) is a solid solution of TiC and TiN, since both TiC and TiN have NaCl structure, the carbon atoms on the TiC superlattice can be replaced by nitrogen atoms in any proportion. Therefore, a continuous series of solid solutions $Ti(C_{1-x},N_x)$ $(0<x<1)$ can be prepared [6]. In general, it is used to improve tool life by combining the properties of tough TiN and hard TiC, so it has various kinds of outstanding properties, for example, high melting point, high hardness, oxidation resistance and high wear resistance. It is widely used to prepare advanced ceramic-based composites employed in metalworking, electrical, electronic, automotive and refractory industries [7,8]. Further improvement of the Ti(C,N) films properties has been investigated by alloying some certain amount of oxygen by various techniques. These improvements observed because of the small atomic size of oxygen and the inertness of oxide, which in turn created high hardness Ti (C, N, O) films [7].

The development of multilayer and nanocomposite heterostructure films allows tailoring material properties to a specific desired value by superlattice and grain size effects [9,10]. Physical and chemical vapor deposition (PVD and CVD) are generally used to deposit films on substrate surfaces [10,11]. CVD is an important process for producing thin films, and is widely used in industry for semiconductors, optoelectronic devices and machining tools. CVD provides an excellent deposition method for uniform hard films.

---

[*] Corresponding author at: Central Metallurgical Research and Development Institute, Advanced Materials Department, El-Felezat street, El-Tebbin, Helwan 11421, Egypt. Tel.: +20 2 25010642; fax: +20 2 25010639.
E-mail address: oafouad@yahoo.com (O.A. Fouad).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.03.030

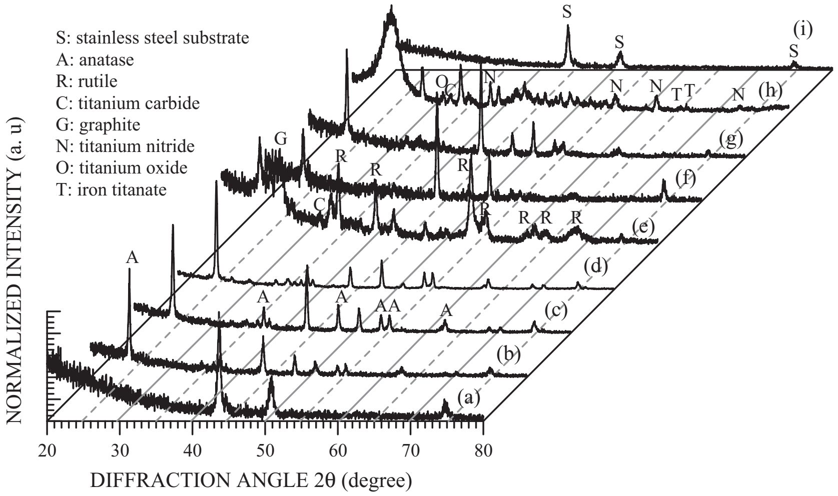

Fig. 1. XRD patterns of the deposited Ti–O–C–N thin films at 350–1000 °C at various experimental conditions. (a) H_2, 350 °C, (b) H_2, 500 °C, (c) H_2, 600 °C, (d) H_2, 750 °C, (e) H_2, 1000 °C, (f) N_2, 600 °C, (g) N_2, 750 °C, and (h) N_2, 1000 °C. The XRD pattern of the steel substrate is shown also for comparison (i).

Although the initial setup cost for CVD is cheaper than that of physical vapor deposition (PVD), control of the CVD process is more complex. Due to complexity in operation, most of the studied CVD systems have been limited to the binary and ternary systems which include TiC, TiN and Ti(C,N) [12].

The CVD of TiO_2, TiC, TiN and their ternary and quaternary thin film systems [13–16] has most often been carried out using volatile titanium tetrachloride ($TiCl_4$) together with reactive gases such as CH_4, H_2, O_2 and N_2. $TiCl_4$ is an air sensitive material and can lead to chlorine contamination of the films and it requires relatively high deposition temperatures [10]. Metal-organic CVD process (MOCVD) using metalorganic precursor have been developed for the low temperature thin films preparation, but they have to be handled very carefully because of their strong tendency to absorb moisture.

In this paper we report on the synthesis of thin films based on Ti–O–C–N binary, ternary and quaternary systems via atmospheric pressure metalorganic CVD or the so-called AP-MOCVD. The structure, composition and morphology of the deposited films with the variation of experimental parameters are also explored.

2. Experimental

2.1. AP-MOCVD system

A home-built atmospheric pressure metalorganic CVD (AP-CVD) system was used in the current study. It consists of three main parts; (i) gas delivery system in which the flowrate of the process gas controlled by a flowmeter; (ii) gas purification system; (iii) tube furnace in which copper turnings heated at 550 °C are used for oxygen removal from process gases. After gas purification there are two flow lines, one line carrying the process gas pass through bubbler contains source material. The bubbler was enveloped by a heating belt with thermocouple and connected to temperature controller type K (model XMTG-2001) which used to heat up the source material to its evaporation point. This bubbler connected by two vacuum valves at the input of the process gas and the output of the precursor vapor. The other line pass directly into the reactor chamber and carrying the Ar gas for flushing the silica tube before and after the experiment; (iv) reactor chamber composed of a tube furnace, inside this furnace a silica tube of 60 cm long and 4 cm outer diameter was inserted. The substrate was set on a ceramic holder and put inside the silica tube at the hot zone. At the other end of the tube the byproducts were vent out.

2.2. Materials

Tetrabutyl orthotitanate ($C_{16}H_{36}O_4Ti$) (TBOT, 97% Fluka), was used as titanium, oxygen and carbon precursors and was introduced into a glass bubbler that set inside an evaporator at temperature of 200 °C during experiments. H_2 acted as a process gas was bubbled through TBOT with a flowrate of 0.2 L/min. The TBOT inputs were controlled by adjusting the temperature of evaporators and amount of H_2 gas passing through it. Substrates were 1 cm × 1 cm stainless steel (SS-316L) pieces. Prior to deposition process, the SS substrates were cleaned with ethanol, distilled water then with acetone. The effect of deposition temperature has been studied in the range of 350–1000 °C. The deposition time varied in the range of 15–90 min. Type of process gas passing through TBOT source such as H_2 or N_2 was also investigated.

2.3. Characterization

The phase composition of the samples were analyzed with X-ray diffraction using Cu-K_α radiation at a scanning speed of 4°/min in the 2θ range from 20° to 80° at room temperature. Scanning electron microscopy were employed to observe the morphologies and grain size of the deposited films. The elemental composition of the films was analyzed with the aid of energy dispersive X-ray analyzer (EDX) unit attached to SEM machine. The chemical states of the Ti, N, O and C in the deposited films were determined by X-ray Photoelectron Spectroscopy using a Mg X-ray source. The survey and high resolution scans were recorded for Ti_{2p}, C_{1s}, O_{1s} and N. The binding energies were compared to the values in the XPS handbook. All peaks were referenced with respect to C_{1s} peak at 284.5 eV. Hardness measurements of the deposited films were performed on the surfaces using Vickers microhardness tester at a load of 50 g.

3. Results and discussion

3.1. Crystal structure and phase analyses

Fig. 1 shows the X-ray diffraction patterns of the deposited Ti–O–C–N thin films on stainless steel substrates using tetrabutyl orthotitanate (TBOT) as metalorganic precursor and H_2 and N_2 as process gases. The flowrate of the gas was 0.2 L/min at substrate temperature 350–1000 °C for deposition time of 30 min. The XRD pattern of stainless steel substrate is also shown there for comparison. It is clear that at lower temperature in presence of hydrogen as a process gas (350 °C, H_2), amorphous Ti–O films deposited, Fig. 1a. As the temperature increased to 500 °C, the diffraction peaks corresponding to Ti–O film are observed. We ascribed the peaks at 2θ of 25.3°, 48° and 37.8° to the anatase (TiO_2) phase (TiO_2-JCPDS card no. 84-1286) which corresponding to (1 0 1), (2 0 0) and (0 0 4) orientations, respectively. The peak intensities are low and has wide feature, Fig. 1b. In addition to anatase phase, peaks of NiFe phase corresponding to steel substrate were also detected. The appearance of the substrate diffraction peaks might be due to discontinuous film and/or deposition of very thin film. It has been reported that thin film of crystalline TiO_2 (anatase phase) were grown at substrate temperature above 480 °C by MOCVD process [12]. It is worthy mentioning that only Ti–O films were deposited using Ar as a process gas under the conditions used for the current study.

The XRD patterns of deposited Ti–O–C films at various substrate temperatures from 600 to 1000 °C using H_2 as a process

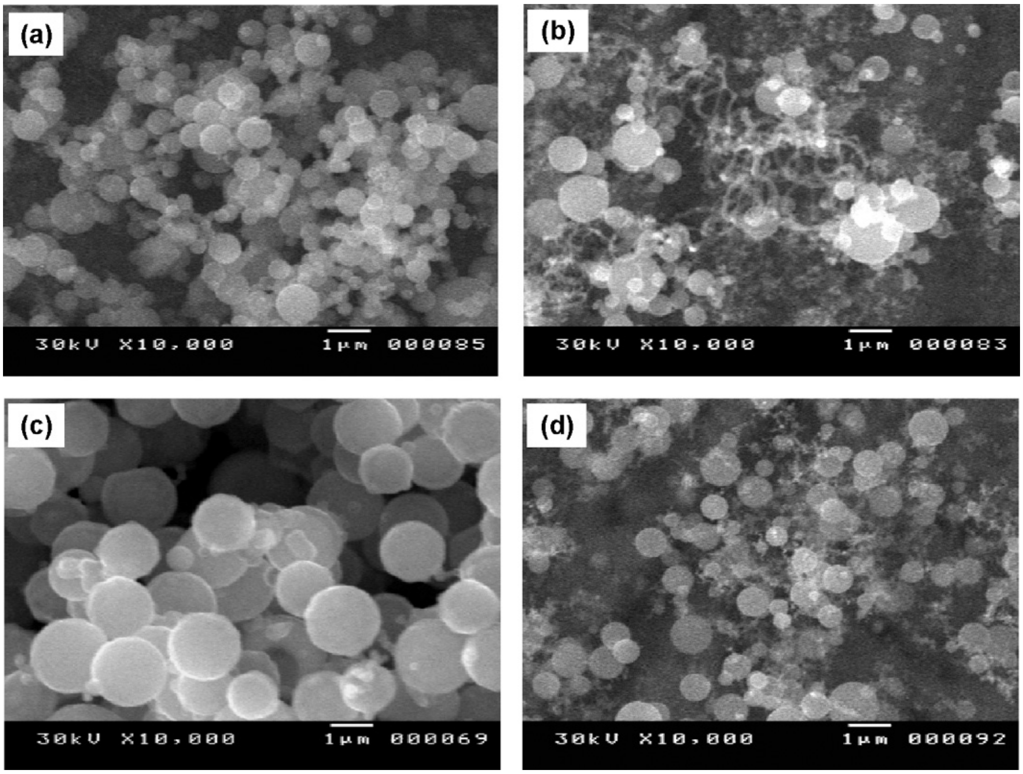

Fig. 2. SEM images of deposited Ti–O–C–N thin films under different gases and at various substrate temperatures, (a) H_2, 500 °C (b) H_2, 600 °C, (c) H_2, 1000 °C, and (d) N_2, 1000 °C.

gas are represented in Fig. 1c–e. As the deposition temperature increased, TiO_2 (anatase) phase grew with preferred orientation (1 0 1), (2 0 0) and (0 0 4) at all temperatures. In addition to the TiO_2 film, peaks corresponding to TiC phase (TiC-JCPDS card no. 65-8803) were also detected at 600 °C with preferred orientation (2 0 0) and (1 1 1) at 2θ values 38.5° and 33.2°, respectively, Fig. 1c. It is well known that the formation of titanium oxide and titanium carbide is thermodynamically favored, as products of metalorganic precursor decomposition in presence of hydrogen gas [16]. However, the intensity of TiC phase is very low compared with that of TiO_2 phase. As the substrate temperature increased to 750 °C, deposition of thicker TiO_2 film on steel substrate and anatase transformation to rutile phase took place (TiO_2-JCPDS card no. 87-0710), Fig. 1d. Anatase is the predominant phase in the sample deposited at 750 °C. Moreover, peaks ascribed to rutile (TiO_2) phase are detected with preferred orientation (1 1 0) and (1 0 1) at 2θ of 27.5° and 36°, respectively. It is clear that the diffraction peaks corresponding to TiC phase are little shifted to higher angles from the standard ones with little broadening at higher deposition temperature (750 °C). This may be attributed to the formation of Ti-oxycarbide (TiOC) phase rather than the formation of single phases (TiC and TiO_2). This means that most probably a solid solution of fcc Ti(C,O)-type phase formed. This means that the film should be substoichiometric, inducing a shift in the diffraction peaks to higher angular positions [17]. Also, it is reported that a Ti-oxycarbide phase formed at the TiC/TiO_2 (rutile) interface, as the substitution of carbon with oxygen in TiC occur without changing the cubic structure of TiC except small change in lattice parameters [18]. Moreover oxygen reacts with the carbide phase according to the following reaction:

$$TiC + yO = TiC_{1-y}O_y + yC[18]$$

By increasing the substrate temperature to 1000 °C, the main XRD peaks are attributed to rutile phase (TiO_2-JCPDS card no. 1-1292) with preferred orientation (2 1 1), (1 1 0), (1 0 1) and (1 1 1) at 2θ of 54.2°, 27.5°, 36° and 41.1°, respectively. It is clear that the intensity of the diffraction peaks corresponding to the anatase phase decreased whereas that corresponding to rutile phase increased at such high temperature, Fig. 1e. It is also observed that the preferred orientation of rutile phase changed with increasing temperature. The variation of textures with deposition temperatures in the CVD processes can be explained by the kinetics of diffusion, absorption and reactions occurred as was observed by other authors [19]. Diminished intensities of TiC peaks is also observed and accompanied with more graphite formation. This indicates that the carbon is replaced by oxygen as a result of Ti–O–C formation. Additionally, the diffraction peaks corresponding to steel substrate (NiFe) still can be detected as the substrate temperature increased. This means that the deposited film is porous (discontinuous) and/or very thin. Meanwhile the oxidation of steel substrate occurred and oxide layer is formed on its surface which react at such high temperature with Ti–O film to form iron titanium oxide ($2FeO{\cdot}TiO_2$) phase. This reaction may also lead to the formation of porous film structure.

XRD patterns of the deposited Ti–O–C–N films at various substrate temperatures using N_2 as a process gas are shown in Fig. 1f–h. At substrate temperature 600 °C, peaks corresponding to Ti_2N phase (Ti_2N-JCPDS card no. 76-0198) are detected with preferred orientation (1 1 1) and (2 2 0) at 2θ of 39.2° and 52.2°, respectively. In addition, the main peaks of TiO_2 (anatase) phase are also can be identified, Fig. 1f. We observed a little broadening of some TiO_2 peaks with diminishing of TiC phase peak intensities as a result of incorporation of nitrogen in the deposited films. The formation of TiN phase can be also confirmed in the deposited film as osbornite with a cubic NaCl structure (JCPDS card no. 65-0970) with preferred orientation (2 0 0), (1 1 1) and (2 2 0) at 2θ of 42.6°, 36.6° and 61.8°, respectively. However, the intensity of TiN peaks is very low compared with that of TiO_2 peaks. The TiN peaks shifted to higher 2

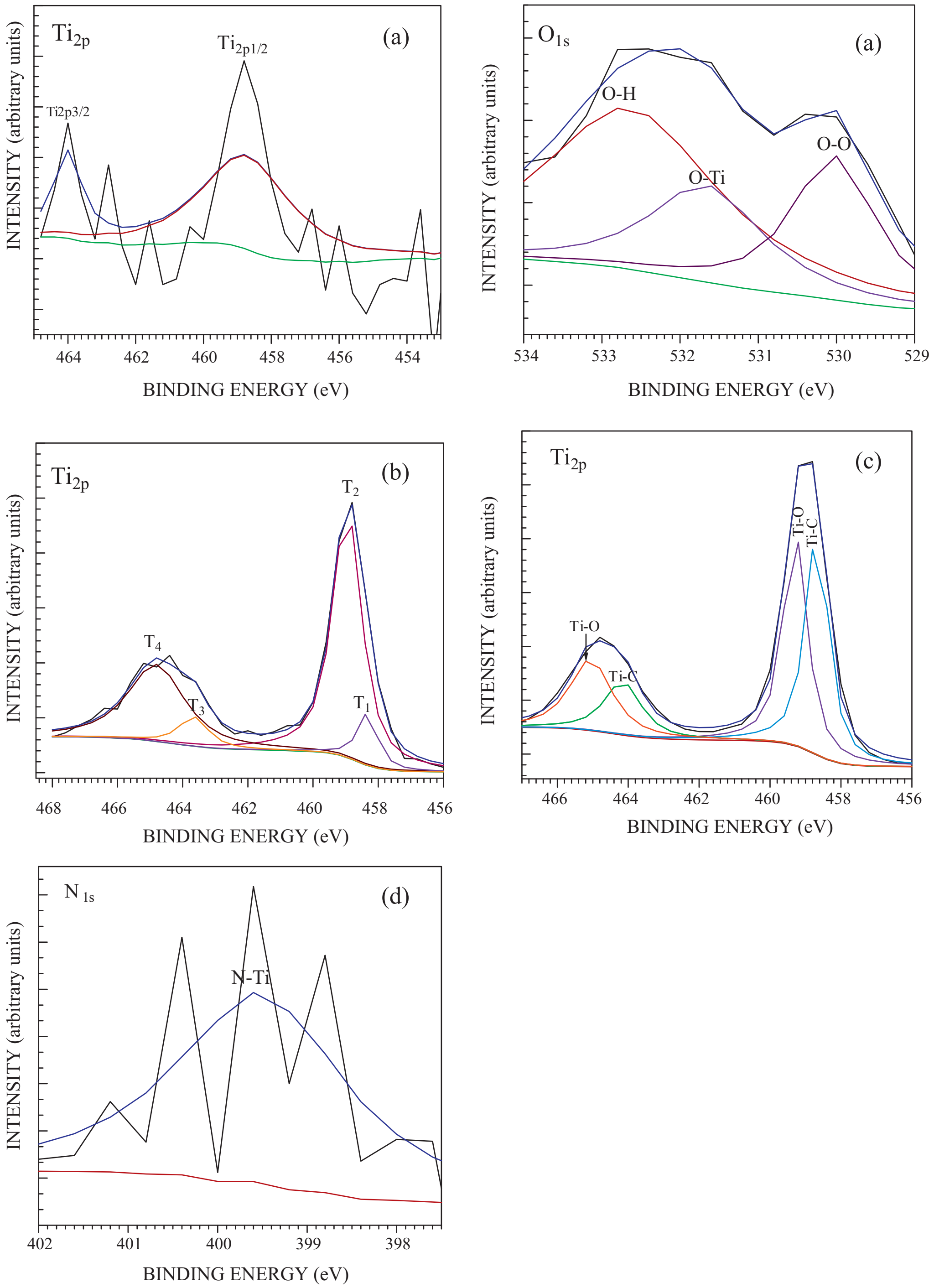

Fig. 3. XPS spectra of Ti_{2P}, O_{1s} and N_{1s} transition of the deposited Ti–O–C–N thin films under various experimental conditions. (a) H_2, 500 °C, (b) H_2, 600 °C, (c) H_2, 750 °C, and (d) N_2, 1000 °C.

theta angles, suggesting solid solution of oxygen in the TiN to form Ti–O–N rather than single phases (TiN and TiO_2) [5,20] for the films deposited at 750 °C. Also, a little shift in TiC peak positions to a higher 2 theta values are observed. This indicates the formation of Ti-oxycarbide phase, Fig. 2g.

Increasing the substrate temperature to 1000 °C, resulted in the transformation of anatase phase to rutile phase and diminishing or decreasing intensities with broadening of the TiO_2 diffraction peaks compared with that in the case of using H_2 as a process gas, Fig. 1h. The intensities of TiN and Ti_2N phases peaks increased and the sharpness of the TiN phase diffraction peaks is observed at 1000 °C substrate temperature. The diffraction peaks corresponding to the iron titanate ($2FeO{\cdot}TiO_2$) phase also appeared as a result of the reaction between steel substrate and titanium oxide at such high temperature. In addition, the peaks ascribed to lower titanium oxide (Ti_3O_5) phase are also detected. This indicates that steel substrate is mainly oxidized due to oxygen diffusion from TiO_2 phase into the substrate surface. Moreover, pairs of TiC and TiN or Ti_2N peaks are observed in the deposited films implying the formation of a solid solution of the two phases [7].

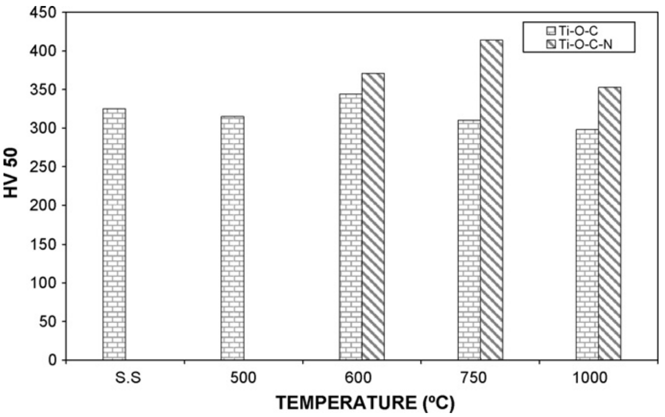

Fig. 4. Vickers hardness of deposited Ti–O–C and Ti–O–C–N thin films as a function of substrate temperature. The value of stainless steel substrate (SS) is also shown for comparison.

3.2. Surface morphology

Fig. 2 shows the SEM images of the deposited thin films at 350–1000 °C in presence of either H_2 or N_2 as process gases. It is found that anatase deposited at 500 °C composed mainly of spherical-like shape particles or grains, Fig. 2a. This spherical-like shape particles are also reported for TiO_2 thin films prepared by other authors [14,15]. The size of these particles is ranged from 300 nm to ~1 μm. It is believed that the micrometer size particles are in fact a coalescence of fine particles of less than 1 μm. This is also supporting that the film follows the grain growth mechanism which are coagulated to form more dense films. The deposited films at 30 min deposition time are discontinuous and porous. By increasing the deposition time to 90 min at substrate temperature of 500 °C, denser TiO_2 film deposited (image not shown here).

The SEM image of deposited Ti(O,C) thin films at 600 °C in presence of H_2 is shown in Fig. 2b. It is clear that in addition to the spherical-like shape particles of TiO_2 (anatase), fiber-like shape structures observe in the sample deposited at 600 °C. By increasing the substrate temperature to 750 °C, size of anatase particles decreased to about 200 nm. It was claimed that the tendency to the decrease of TiC grain size with the increase of oxygen flowrate was accompanied by a significant peak broadening as a result of transformation of TiC to Ti-oxycarbide [20]. Also, at that temperature (750 °C) we observed disappearance of fiber-like shape structures which appeared at 600 °C and the morphology of the deposited film was mainly spherical-like shape particles. At 1000 °C deposition temperature, catalytic growth of spherical particles occurred with increase in particle size to >1 μm took place (Fig. 2c). This may be due to reaction of steel substrate with deposited film and transformation of anatase to rutile phase (main peaks).

SEM images of Ti–O–C–N thin film deposited at 600 °C deposition temperature in presence of N_2 as a process gas, illustrated the disappearance of fiber-like shape structures in the sample deposited at 600 °C, which related to TiC phase as detected in case of using H_2 as a process gas. Caschera et al. also did not detect any TiC phase in the deposited film using metalorganic precursor at low temperatures in absence of H_2 gas [16]. These results support the formation of single phase (Ti-oxycarbide) rather than multiple phases (TiO_2 and TiC) as mentioned before. By increasing substrate temperature to 1000 °C, observable catalytic growth occurred as the crystal size increased to about 5 μm. The particles increased in size and become more round in shape with increasing flowrate and incorporation of more nitrogen into the deposited films as was observed by other authors [7].

3.3. Chemical composition and states

Fig. 3 shows the Ti_{2p}, O_{1s} and N_{1s} XPS spectra [21,22] of deposited Ti–O–C–N thin films that shown in Fig. 1. The binding energy due to $Ti_{2P1/2}$ and $Ti_{2P3/2}$ of TiO_2 phase are detected at 458.8 and 464 eV, respectively, Fig. 3a. The O_{1s} XPS spectra show peaks at 531.6 eV and 532.4 eV, respectively. The peak at 531.6 eV is assigned to oxygen bound to tetravalent Ti ions. Whereas the peak at 532.4 eV implies that the surface is partially covered with hydroxide OH groups, Fig. 3a [1]. It is worthy mentioning that, the oxygen composing the films is expected to be originated mainly from precursor since we used a very tight system and pure H_2 gas as a reactive gas.

The XPS spectra of the Ti_{2p} transition can be fitted by four Gaussian functions for the deposited films at 600 °C. Ti showed four peaks at 458 (T_1), 458.8 (T_2), 463.6 (T_3) and 464.4 eV (T_4), respectively (Fig. 3b). The T_1 and T_2 peaks write to the $Ti_{2P3/2}$ splitting, and T_3 and T_4 are their relevant $Ti_{2P1/2}$ splitting. In this film Ti has two oxidation states, T_1 which related to Ti–C bond and T_2 related to Ti–O bond [3]. These results are in agreement with the XRD results for deposited film at 600 °C where titanium carbide peaks were detected.

For the deposited films at 750 °C, titanium showed two peaks. The $Ti_{2p3/2}$ peak at 459.2 eV and $Ti_{2p1/2}$ at 464.8 eV which assigned to Ti–O bond formation, Fig. 3c. In addition, Ti_{2p} has two other peaks at 458.8 eV and at 464 eV which related to Ti–C bond formation. This indicates that oxygen might be incorporate into the grain boundaries of TiC rather than the formation of oxide phase. On the other hand, the XPS spectra (not shown here) of the Ti_{2p}, C_{1s} and O_{1s} regions are similar to that of the Ti–O–C films. The XPS spectrum of N_{1s} transition for the Ti–O–C–N films showed the main peak at 399.6 eV which assigned to Ti–N bond formation, Fig. 3d. The atomic composition of this film implying that it contains 51.9% C, 33.8% O and 12.6% Ti. This result indicates that we obtained a nonstoichiometric film and not a stoichiometric one. This might be due to the fact that carbon and oxygen atoms can replace each other in the lattice based on their partial pressures and/or reaction conditions.

3.4. Hardness of deposited films

Microhardness measurements of deposited Ti–O–C–N films at various substrate temperatures are represented in Fig. 4. Ti–O–C films showed a significant increase in hardness value of sample deposited at 600 °C (~350 HV_{50}) than that deposited at 1000 °C (~300 HV_{50}). This might be due to the deposition of TiC phase in this sample. The structural changes induced by changing substrate temperature is the major reason for the decrease in the hardness of the films deposited at 750 °C (~310 HV_{50}) and 1000 °C (~300 HV_{50}). This decrease in hardness resulting from the increase in the oxide phases amount as a result of formation and anatase transformation to rutile phase and oxidation of TiC. Fernandes et al. [20] observed that TiC has higher hardness value than that of Ti-oxycarbide with increasing oxygen flowrate. High hardness value at 600 °C also may be related to the amorphous carbon existed at the grain boundaries of the TiC grains.

For Ti–O–C–N films the samples deposited at 600 °C and 750 °C showed higher hardness values than that for Ti–O–C films (~360 HV_{50} and ~425 HV_{50}, respectively). This might be due to the formation of Ti-nitride phase(s). The decrease of hardness value for sample deposited at 1000 °C, although its value is still higher than that of steel substrate, might be due to the continuous amorphization tendency in the deposited film.

It is worthy mentioning that the represented hardness values in Fig. 4 of the deposited films are the average of three readings at different points. It is also expected that these values are dependent on the film composition. However, in case of Ti–O–C–N films, it is expected to have higher hardness at all ratios of N_2 additions. This is because that the prepared Ti–O–C films showed higher hardness than the prepared TiO_2 film. By the addition of N-atoms to the film, the hardness suppose to increase since Ti_xN_y phase will be of higher hardness than that of TiO_2 and TiC.

4. Conclusion

Ti(O,C,N) thin films were synthesized using metalorganic TBOT precursor from the vapor phase via APCVD process. Crystalline TiO_2 (anatase) phase thin films with particle size of about 300 nm were successfully deposited at substrate temperature higher than 400 °C as spherical-like shape particles using TBOT as a precursor. The results supported that TiO_2 and TiC deposition were thermodynamically favored as products of metalorganic precursor decomposition in presence of H_2 gas at temperature >500 °C. Whereas TiO_2 deposited in the form of spherical-like shape particles, TiC deposited in the form of fiber-like shape structures. Ti-oxycarbide phase detected at 750 °C as a result of carbon segregation and reaction of oxygen with TiC phase. Formation of TiN and Ti_2N phases was observed in case of using N_2 as a process gas even at lower deposition temperature (600 °C). Higher hardness ($\sim$350 HV_{50}) for Ti–O–C film was obtained for sample deposited at 600 °C due to the formation of TiC phase. Whereas high hardness value was obtained for Ti–O–C–N films at 750 °C ($\sim$425 HV_{50}) due to the formation of stoichiometric TiN phase.

References

[1] A.C. Gallardo, M. Guerrero, N. Castillo, A.B. Soto, R. Fragoso, J.G. Cabanas-Moreno, Thin Solid Films 473 (2005) 68.
[2] O.A. Fouad, A.K. Rumaiz, S.I. Shah, Thin Solid Films 517 (2009) 5689.
[3] L. Tong, R.G. Reddy, Scripta Mater. 52 (2005) 1253.
[4] J.C. Nable, S. Nosheen, S.L. Suib, F.S. Galasso, Surf. Coat. Technol. 200 (2006) 2821.
[5] S. Shimada, Y. Takada, J. Tsujino, Surf. Coat. Technol. 199 (2005) 72.
[6] D. Xiang, Y. Liu, Z. Zhao, H. Cao, S. Gao, M. Tu, J. Alloys Compd. 429 (2007) 264.
[7] J.H. Hsieh, C. Li, W. Wu, A.L.K. Tan, J. Mater. Process. Technol. 140 (2003) 662.
[8] D. Xiang, Y. Liu, S. Gao, M. Tu, Mater. Charact. 59 (2008) 241.
[9] J.C. Sanchez-Lopez, D. Martinez, C.L. Cartes, A. Fernandez, Surf. Coat. Technol. 202 (2008) 4011.
[10] O.A. Fouad, M. Yamazato, M. Era, M. Nagano, T. Hirai, I. Usui, J. Cryst. Growth 234 (2002) 440.
[11] M. Takahashi, S. Shimada, Solid State Ionics 172 (2004) 249.
[12] D.H. Kuo, K.W. Huang, Thin Solid Films 394 (2001) 81.
[13] K. Shalini, S. Chandrasekaran, S.A. Shivashankar, J. Cryst. Growth 284 (2005) 388.
[14] B.H. Kim, J.Y. Lee, Y.H. Choba, M. Higuchi, N. Mizutani, Mater. Sci. Eng. B107 (2004) 289.
[15] B. Arvan, A. Khakifirooz, R. Tarighat, S. Mohajerzadeh, A. Goodarzi, E.A. Soleimani, E. Arzi, Mater. Sci. Eng. B109 (2004) 17.
[16] D. Caschera, F. Federici, S. Kaciulis, L. Pandolfi, A. Cusma, G. Padeletti, Mater. Sci. Eng. C27 (2007) 1328.
[17] A.C. Fernandes, P. Carvalho, F. Vaz, S.L. Mendez, A.V. Machado, N.M.G. Parreira, J.F. Pierson, N. Martin, Thin Solid Films 515 (2006) 866.
[18] A. Belluci, D. Gozzi, A. Latini, Solid State Ionics 172 (2004) 369.
[19] D.H. Kuo, K.W. Huang, Thin Solid Films 394 (2001) 72.
[20] A.C. Fernandes, F. Vaz, L. Cunha, N.M.G. Parreira, A. Cavaleiro, Ph. Goudeau, E. Le Bourhis, J.P. Riviere, D. Munteanu, B. Borcea, R. Cozma, Thin Solid Films 515 (2007) 5424.
[21] P. Stefanov, M. Shipochka, P. Stefchev, Z. Raicheva, V. Lazarova, L. Spassov, J. Phys. 100 (2008), 012039.
[22] G. Soto, Appl. Surf. Sci. 233 (2004) 115.