JOURNAL OF MATERIALS SCIENCE 28 (1993) 6446–6449

Deposition rates of titanium nitride plates prepared by chemical vapour deposition of $TiCl_4 + NH_3$ system

C.-C. JIANG, T. GOTO, T. HIRAI
Institute for Materials Research, Tohoku University, Sendai 980, Japan

Titanium nitride plates (TiN_x, $x = 0.74$–1.0, about 2 mm thick maximum) were prepared by chemical vapour deposition (CVD) using $TiCl_4$, NH_3 and H_2 as source gases. The effects of CVD conditions, i.e. gas molar ratio ($m_{N/Ti} = NH_3/TiCl_4$) and deposition temperature (T_{dep}), on deposition rates and surface morphology were examined, and the deposition mechanism of the CVD-TiN_x plates was discussed. The relationship between $m_{N/Ti}$ and deposition rates showed a maximum peak at certain $m_{N/Ti}$, and this maximum peak shifted to lower $m_{N/Ti}$ with increasing T_{dep}. The activation energy for the formation of CVD-TiN_x plates was about 80 kJ mol^{-1} in the lower temperature range. The decomposition reaction of NH_3 gas could be associated with the rate-controlling step. At higher temperatures, the diffusion process may be the rate-controlling step, and a large amount of powder (mainly NH_4Cl) was formed in the gas phase. The highest deposition rate obtained in the present work was 1.06×10^{-7} m s^{-1} (0.38 mm h^{-1}) at $T_{dep} = 1773$ K and $m_{N/Ti} = 0.87$.

1. Introduction

Titanium nitride (TiN_x) film is widely used as a coating for tools owing to its erosion/corrosion resistance and good compatibility with metals, and as decorative coatings owing to its colour similar to gold [1].

There are several methods, such as sputtering, ion-plating and chemical vapour deposition (CVD), for the preparation of TiN_x films. CVD is advantageous to obtain high-purity and high-density films at high deposition rates. The CVD conditions, such as deposition temperature, source gas ratio, gas flow rate and total gas pressure, should be optimized for the highest deposition rates.

$TiCl_4$ is commonly used as the titanium source, and either NH_3 or N_2 gas may be chosen as the nitrogen source for preparing TiN_x by CVD. The $TiCl_4 + N_2$ system has been employed in many reports [2–7], because NH_3 gas was thought to be too active to control the CVD process.

We have prepared CVD-TiN_x plates whose composition (x = N/Ti) ranged between 0.74 and 1.0 by using the $TiCl_4 + NH_3$ system [8]. In the present work, the effects of CVD conditions on deposition rates and surface morphology were investigated, and the optimum conditions for the highest deposition rate were obtained. The deposition mechanism of the CVD-TiN_x plates was also discussed.

2. Experimental procedure

A cold-wall type CVD chamber was used to prepare TiN_x plates on graphite substrates using $TiCl_4$, NH_3 and H_2 gases as source materials. The detailed experimental apparatus and the procedure were reported elsewhere [8]. Deposition temperature, T_{dep}, ranged from 1373–1873 K, the molar ratio of $TiCl_4$ to NH_3 in the source gas ($m_{N/Ti} = NH_3/TiCl_4$) was controlled between 0.17 and 1.74. Total gas pressure, P_{tot}, was kept at 4 kPa. When $P_{tot} > 4$ kPa, temperature measurements using a two-colour optical pyrometer could not be properly taken due to heavy powder (mainly NH_4Cl) formation in the gas phase.

The surface texture of the CVD-TiN_x plates was observed by SEM. The thickness was measured using an optical microscope. The deposition rates were calculated from x/t (x = thickness, t = time) because of the linear relationship between thickness and time.

3. Results and discussion

Fig. 1 shows the relationship between $m_{N/Ti}$ and deposition rates of CVD-TiN_x plates. Maximum peaks were observed, and the peak shifted to lower $m_{N/Ti}$ with increasing T_{dep}. In the lower $m_{N/Ti}$ region, the deposition rates increased linearly with increasing NH_3 gas molar ratio. Saeki *et al.* [9] prepared TiN_x powder by CVD using the $TiCl_4 + NH_3$ system and reported a large amount of NH_4Cl powder formation in the reaction chamber. In the present work, the depletion of NH_3 concentration due to the powder (NH_4Cl) formation in the gas phase may be the main reason for the decrease of deposition rates at higher $m_{N/Ti}$ and T_{dep} region. Similar behaviour was reported in CVD-BN [10] and CVD-Si_3N_4 [11] prepared by the metal halide + NH_3 system where by-product powders, such as NH_4Cl and $Si(NH_2)_4$, were formed.

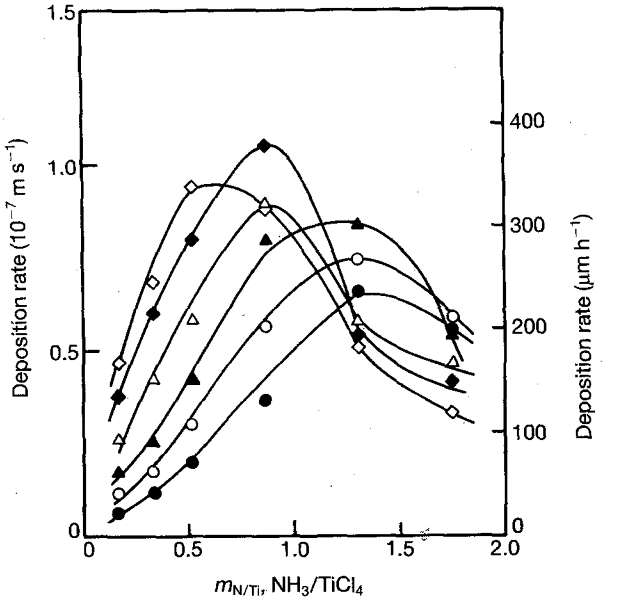

Figure 1 Effect of $m_{N/Ti}$ on the deposition rates of CVD-TiN$_x$ plates. T_{dep} (K): (◇) 1873, (◆) 1773, (△) 1673, (▲) 1573, (○) 1473, (●) 1373.

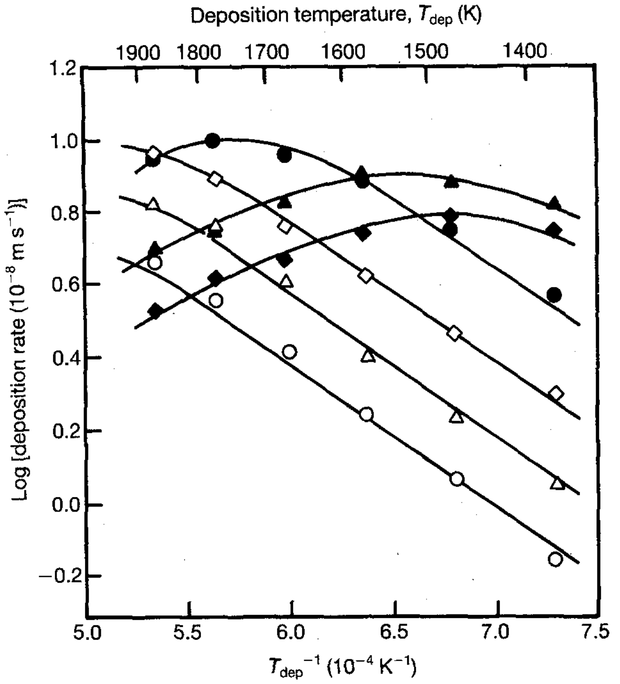

Figure 2 Arrhenius plot of the deposition rates for the CVD-TiN$_x$ plates. $m_{N/Ti}$: (○) 0.17, (△) 0.34, (◇) 0.52, (●) 0.87, (▲) 1.30, (◆) 1.74.

TABLE I Activation energy for the deposition of CVD-TiN$_x$ films

Source gases	Activation energy (kJ mol^{-1})	Deposition temperature (K)	Reference
TiCl$_4$ + N$_2$ + H$_2$	309	1173–1273	[2]
	39	1273–1423	[2]
	48	1273–1373	[3]
	51	1173–1373	[4]
	84	1200–1400	[5]
	86	1073–1473	[6]
	91	1073–1273	[7]
TiCl$_4$ + NH$_3$ + H$_2$	80	1373–1573	Present work

Fig. 2 demonstrates the Arrhenius plot of the deposition rates for the CVD-TiN$_x$ plates. The deposition rates increased with increasing T_{dep} in the $m_{N/Ti}$ range between 0.17 and 0.52. The relationship between log (deposition rate) versus $1/T_{dep}$ was linear, and the activation energy was about 80 kJ mol^{-1}. When $m_{N/Ti} > 1.3$, the deposition rates were almost constant or slightly decreased with increasing T_{dep}. This is a well-known trend of CVD, and can be explained as the diffusion-controlled kinetics and homogeneous reactions (powder formation) in the gas phase [12].

Table I summarizes activation energies for the deposition of CVD-TiN$_x$ films given in the literature. Kim and Chun [2], Cho *et al.* [3] and Sadahiro *et al.* [4] reported values from 39–51 kJ mol^{-1}. They concluded that the rate-controlling step for the deposition of CVD-TiN$_x$ films could be diffusion of source gases in the gas phase. On the other hand, Teyssandier *et al.* [5], Takahashi and Suzuki [6], Brekel *et al.* [7] and Kim and Chun [2] obtained activation energies between 84 and 309 kJ mol^{-1}. These higher activation energy values suggest that the rate-controlling step may be chemical reactions at the substrate surface. The activation energy obtained in the present work, 80 kJ mol^{-1}, was almost in agreement with those reported by Teyssandier *et al.* [5] and Takahashi and Suzuki [6]. The deposition rates increased linearly with increasing NH$_3$ gas molar ratio in the lower $m_{N/Ti}$ region (see Fig. 1). The rate-controlling step in the present work may be chemical reactions with which decomposition of NH$_3$ gas may be associated.

Fig. 3 shows the effect of $m_{N/Ti}$ on the surface morphology of CVD-TiN$_x$ plates. The surface texture changed, mainly depending on $m_{N/Ti}$, from faceted to nodular with increasing $m_{N/Ti}$.

The relationship between deposition mechanism and surface morphology was discussed by Holman and Huegel for CVD-W/WRe [13] and by Hirai *et al.* for CVD-SiC [14]. It is known that faceted and nodular textures are observed under reaction-controlled and diffusion-controlled conditions, respectively. In the present work, the faceted and nodular textures were observed at lower $m_{N/Ti}$ (reaction-controlled) and higher $m_{N/Ti}$ (diffusion controlled) region, respectively (see Fig. 3). This is in agreement with the general trend mentioned above.

Fig. 4 summarizes the deposition rates of CVD-TiN$_x$ films reported so far. It seems that the deposition rates by the cold-wall type CVD are larger than those by hot-wall type CVD. Premature reactions in the gas phase or by-product (powder) formation at the wall surface of the CVD chamber are more significant in the hot-wall type CVD. The reaction zone in the cold-wall type CVD is restricted near to substrates; therefore, fresh source gases are transported to the substrate, and therefore the deposition efficiency must be improved.

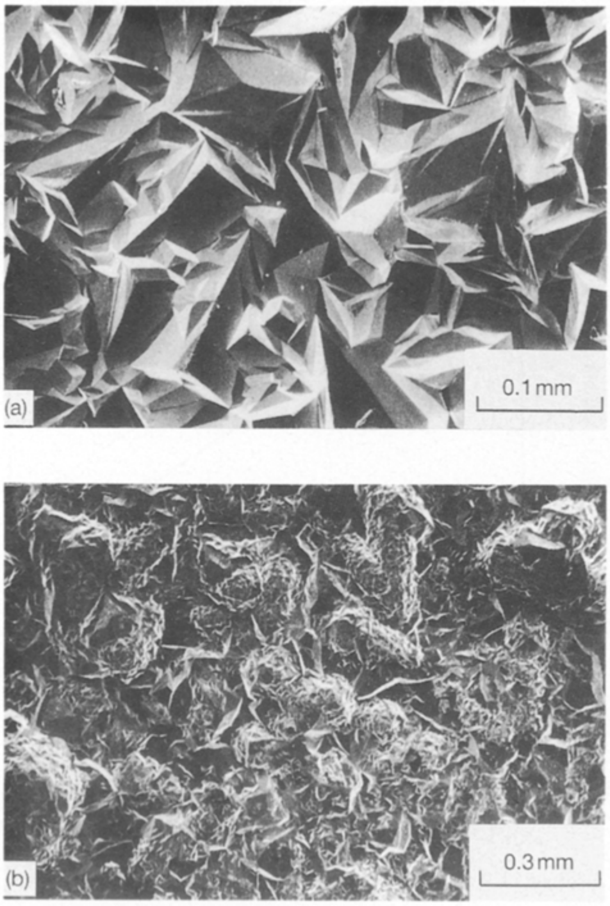

Figure 3 Surface texture of CVD-TiN$_x$ plates. (a) $m_{N/Ti} = 1.04$, (b) $m_{N/Ti} = 1.30$, ($T_{dep} = 1773$ K).

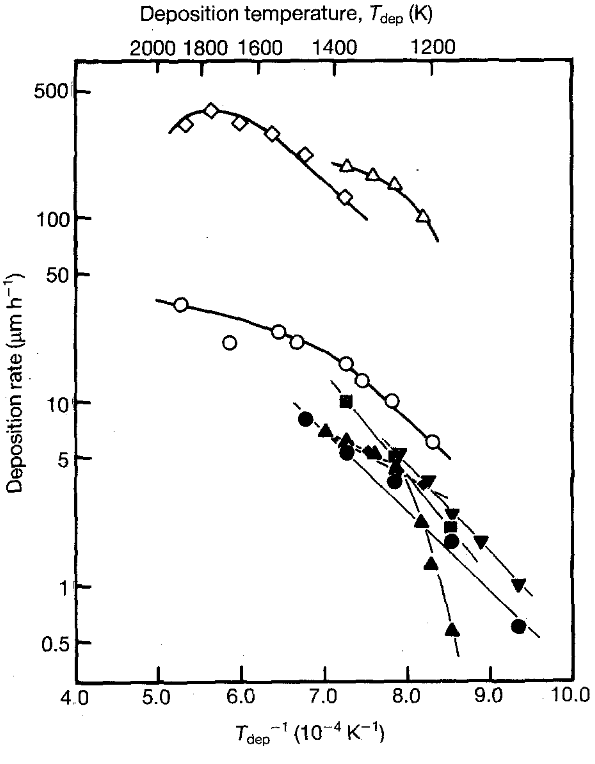

Figure 4 Comparison of deposition rates between present work and previously reported values. Hot-wall type CVD: (▲) [2], (◆) [3], (▼) [4], (■) [6], (●) [7]. Cold-wall type CVD: (○) [5], (△) [15], (◇) present work. $TiCl_4 + N_2$ system: (▲) [2], (◆) [3], (▼) [4], (○) [5], (■) [6], (●) [7], (△) [15]. $TiCl_4 + NH_3$ system: (◇) present work.

The highest deposition rate obtained in the present work was 1.06×10^{-7} m s^{-1} (0.38 mm h^{-1}) at $T_{dep} = 1773$ K, $m_{N/Ti} = 0.87$. This value is about several tens of times larger than reported values. The introduction of NH_3 gas (which is more active than N_2 gas) through a double-tube nozzle (which prevents premature reactions) into the cold-wall type CVD chamber must have enabled the highest deposition rate.

4. Conclusions

TiN$_x$ plates (up to 2 mm thick) were prepared by cold-wall type CVD under the condition of $T_{dep} = 1373$–1873 K, $P_{tot} = 4$ kPa, $m_{N/Ti} = 0.17$–1.74 using $TiCl_4$, NH_3 and H_2 as source gases. The following results were obtained.

1. In the lower $m_{N/Ti}$ region, the deposition rates increased with increasing $m_{N/Ti}$ and T_{dep}. The activation energy was about 80 kJ mol^{-1}. Decomposition of NH_3 gas could be associated with the rate-controlling step of the deposition of CVD-TiN$_x$ plates.
2. In the higher $m_{N/Ti}$ region, the deposition rates decreased with increasing $m_{N/Ti}$, and were almost constant or slightly decreased with increasing T_{dep}. A large amount of powder (mainly NH_4Cl) formation was observed. The rate-controlling step may be the diffusion process in the gas phase.
3. The highest deposition rate obtained in the present work was 1.06×10^{-7} m s^{-1} (0.38 mm h^{-1}) at $T_{dep} = 1773$ K and $m_{N/Ti} = 0.87$. This value is about several tens of times larger than reported values.
4. The surface texture of CVD-TiN$_x$ plates was "faceted" in the low T_{dep}, low $m_{N/Ti}$ (reaction-controlled) region, and was "nodular" in the high T_{dep}, high $m_{N/Ti}$ (diffusion-controlled) region.

Acknowledgement

This research was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture under Contracts 02203105 and 63850149.

References

1. M. E. SJOSTRAND, in "Proceedings of 7th International Conference on Chemical Vapour Deposition", edited by T. O. Sedgwick and H. Lydtin (Electrochemical Society, Princeton, NJ, 1979) p. 452.
2. M. S. KIM and J. S. CHUN, *Thin Solid Films* **107** (1983) 129.
3. J. S. CHO, S. W. NAM and J. S. CHUN, *J. Mater. Sci.* **17** (1982) 2495.
4. T. SADAHIRO, T. CHO and S. YAMAYA, *J. Jpn Inst. Metals* **41** (1977) 542.
5. F. TEYSSANDIER, C. BERNARD and M. DUCARROIR, in "Proceedings of the 6th European Conference on Chemical Vapour Deposition", edited by R. Porat (Iscar, Jerusalem, 1987) p. 96.
6. T. TAKAHASHI and Y. SUZUKI, *Nippon Kagaku Kaisi* **6** (1974) 1043.
7. C. H. J. VAN DEN BREKEL, R. M. M. FONVILLE, P. J. M. VAN DER STRATEN and G. VERSPUI, in "Proceedings of the 8th International Conference on Chemical Vapour Deposition", edited by J. M. Blocher, Jr., J. Wahl and G. E. Vuillard (Electrochemical Society, Princeton, NJ, 1981) p. 142.

8. C. C. JIANG, T. GOTO and T. HIRAI, *J. Mater. Sci.* in press.
9. Y. SAEKI, R. MATSUZAKI, A. YAJIMA and M. AKIYAMA, *Bull. Chem. Soc. Jpn* **55** (1982) 3193.
10. T. MATSUDA, H. NAKAE and T. HIRAI, *J. Mater. Sci.* **23** (1988) 509.
11. K. NIIHARA and T. HIRAI, *ibid.* **11** (1976) 593.
12. W. A. BRYANT, *ibid.* **12** (1977) 1285.
13. W. R. HOLMAN and F. J. HUEGEL, *J. Vac. Sci. Technol.* **11** (1974) 701.
14. T. HIRAI, T. GOTO and T. KAJI, *Yogyo-Kyokai-Shi* **91** (1983) 502.
15. T. TAKAHASHI and H. ITOH, *J. Electrochem. Soc.* **124** (1977) 797.

Received 25 June 1992
and accepted 20 April 1993