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Non-stoichiometry of titanium nitride plates prepared by chemical vapour deposition

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Abstract

Wide-ranging non-stoichiometric titanium nitride (TiN_x) plates ($x=0.74$–1.0) were prepared by chemical vapour deposition from a $TiCl_4$–NH_3–H_2 system. The lattice parameter increased from 0.4228 to 0.4240 nm with increasing x. The density changed in the range between 5.1 and 5.4×10^3 kg m^{-3}, which is in agreement with theoretical values calculated from the lattice parameters and the compositions. The deposition domains of non-stoichiometric TiN_x were calculated thermodynamically as a function of input composition. The deposition mechanism of the non-stoichiometric TiN_x plates was discussed by comparing the calculations with experimental results.

1. Introduction

Titanium nitride (TiN_x) films have been applied as coatings for tools because of their superior mechanical properties and as decorative coatings because of their gold-like colour [1]. TiN_x has wide-ranging non-stoichiometric compositions with x between 0.5 and 1.0 [2], which must strongly affect its properties. Therefore it is important to investigate the relationship between the properties and the non-stoichiometry of TiN_x films, and to prepare well-controlled non-stoichiometric TiN_x films.

Several methods including sputtering, ion plating and chemical vapour deposition (CVD) have been used to prepare TiN_x films, and CVD is advantageous for obtaining pure and dense films at high deposition rates. Teyssandier *et al.* [3] prepared wide-ranging non-stoichiometric TiN_x films by CVD using the $TiCl_4$–N_2–H_2 system. However, the relationship between the non-stoichiometry and the properties was not reported because their films seem to be too thin to measure several properties.

We have prepared highly pure dense TiN_x plates (up to 2 mm thick) at a high deposition rate of about 0.4 mm h^{-1} by CVD using the $TiCl_4$–NH_3–H_2 system [4]. In the present work, the effects of CVD conditions on the composition, lattice parameter and density were investigated. The deposition domains of non-stoichiometric TiN_x were calculated thermodynamically as a function of input composition. The deposition mechanism of the CVD TiN_x plates was speculated about by comparing the calculations and experimental results.

2. Calculation

The optimization method which minimizes the total Gibbs free energy was used to calculate the thermodynamic equilibrium state. The computer code SOLGASMIX-PV developed by Besmann [5] was applied to the calculation in which 18 gaseous species and two solid species were considered. The gaseous and solid species used in the present calculation are summarized in Table 1. The thermodynamic data for the gaseous species were taken from ref. 6. The Gibbs free energy function for TiN_x expressed as an equation in x given by Teyssandier *et al.* [3] was employed.

3. Experimental details

CVD TiN_x plates were prepared on graphite substrates using $TiCl_4$, NH_3 and H_2 gases as the source materials. The substrates were heated by transmitting an electric current. The detailed preparation set-up and procedure have been reported elsewhere [4]. The deposition temperature T_{dep} ranged from 1373 to 1873 K, and the

TABLE 1. Chemical species in the Ti–N–H–Cl system

Gas species					
Ti	N	H	Cl	NH	NH_2
NH_3	N_2	H_2	Cl_2	N_3	N_2H_2
N_2H_4	HCl	TiCl	$TiCl_2$	$TiCl_3$	$TiCl_4$
Solid species					
Ti	TiN_x				

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source gas molar ratio $m_{N/Ti}$ (= [NH$_3$]/[TiCl$_4$]) was varied between 0.17 and 1.74. The total gas pressure P_{tot} was fixed at 4 kPa. Above $P_{tot} = 4$ kPa, T_{dep} was not measurable with an optical pyrometer owing to heavy powder formation in the gas phase. When $T_{dep} > 1773$ K, TiC layers were formed at the interfaces between the CVD TiN$_x$ plates and the graphite substrates. The TiC layers were completely removed from the deposits before the characterizations.

The lattice parameters were investigated using an X-ray diffractometer (Rigaku RAD-C; nickel-filtered Cu Kα) using silicon as an internal standard material. The density was examined by the Archimedes method of immersion in toluene. The titanium and nitrogen contents were determined by inductively coupled plasma analysis (Seiko Electric SPS 1200A) and chemical analyses. Electron probe microanalysis (EPMA) (Shimadzu EMX) was applied to detect oxygen impurities.

4. Results and discussion

Figure 1 shows the effect of $m_{N/Ti}$ on the lattice parameters of CVD TiN$_x$ plates. The lattice parameter increased with increasing $m_{N/Ti}$ and T_{dep} in the $m_{N/Ti}$ range between 0.17 and 1.0 and was almost constant when $m_{N/Ti} > 1.0$.

Figure 2 depicts the effect of $m_{N/Ti}$ on the nitrogen-to-titanium atomic ratio of the CVD TiN$_x$ plates. The trend is the same as that of the lattice parameter shown in Fig. 1.

Figure 3 demonstrates the deposition domains of non-stoichiometric TiN$_x$ calculated as a function of the input composition, *i.e.* TiCl$_4$ and NH$_3$ partial pressures.

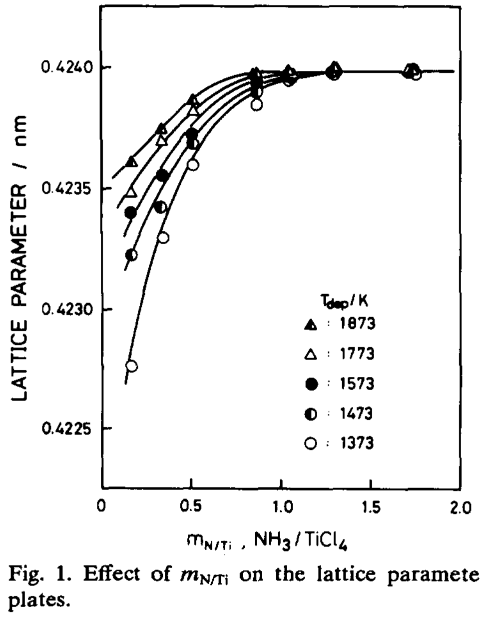

Fig. 1. Effect of $m_{N/Ti}$ on the lattice parameters of CVD TiN$_x$ plates.

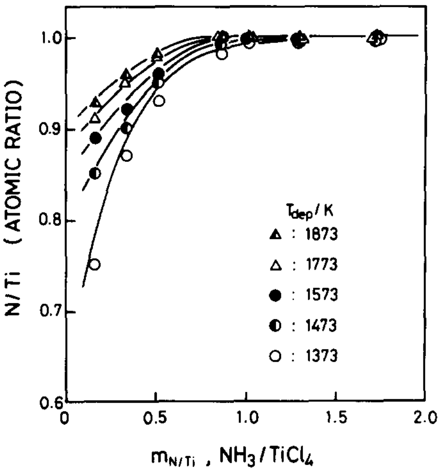

Fig. 2. Effect of $m_{N/Ti}$ on the nitrogen-to-titanium atomic ratio of CVD TiN$_x$ plates.

It is seen that the non-stoichiometry may be controlled over wide ranges, and the deposition region of non-stoichiometric TiN$_x$ becomes smaller at higher T_{dep} conditions.

The calculated and experimental deposition domains for non-stoichiometric TiN$_x$ are represented in Fig. 4. Although the calculations and experiments have the same trend, *i.e.* x values increase with increasing $m_{N/Ti}$, there is a significant discrepancy between the calculated and the experimental $m_{N/Ti}$ values for the deposition of non-stoichiometric TiN$_x$ plates.

Teyssandier *et al.* [3] demonstrated thermodynamic calculations for the deposition of non-stoichiometric TiN$_x$ films by CVD from the TiCl$_4$–N$_2$–H$_2$ system and compared them with their experimental results. Figures 3(a) and 3(b) are similar to their calculations. However, Fig. 3(c) shows a relatively wider "no-deposit" region than theirs. This may be caused by the different source gases or the different total amount of source gases assumed in the calculation.

By using CVD from the TiCl$_4$–N$_2$–H$_2$ system, Kato and Tamari [7] prepared TiN$_x$ films at $T_{dep} = 1473$–1573 K, $P_{tot} = 0.1$ MPa and $m_{N/Ti} = 1.4$–60, and Kato *et al.* [8] prepared TiN$_x$ powders at $T_{dep} = 973$–1773 K, $P_{tot} = 0.1$ MPa and $m_{N/Ti} = 1.2$–1.4. Both reports proposed the same formation mechanism, namely that TiCl$_4$ gas is initially reduced into metallic titanium and then the metallic titanium reacts with N$_2$ gas to form TiN$_x$. Teyssandier *et al.* [3] also presented the same idea as the above-mentioned mechanism according to their thermodynamic calculations in the case when $P_{tot} = 0.1$ MPa, while for $P_{tot} < 0.1$ MPa they suggested another mechanism, *i.e.* direct reaction between TiCl$_4$ and N$_2$ gases. The gas phase reaction of NH$_3$ must be more likely than that of N$_2$ because NH$_3$ gas is more active than N$_2$ gas. The discrepancy between the experiments and calculations in the present work (see

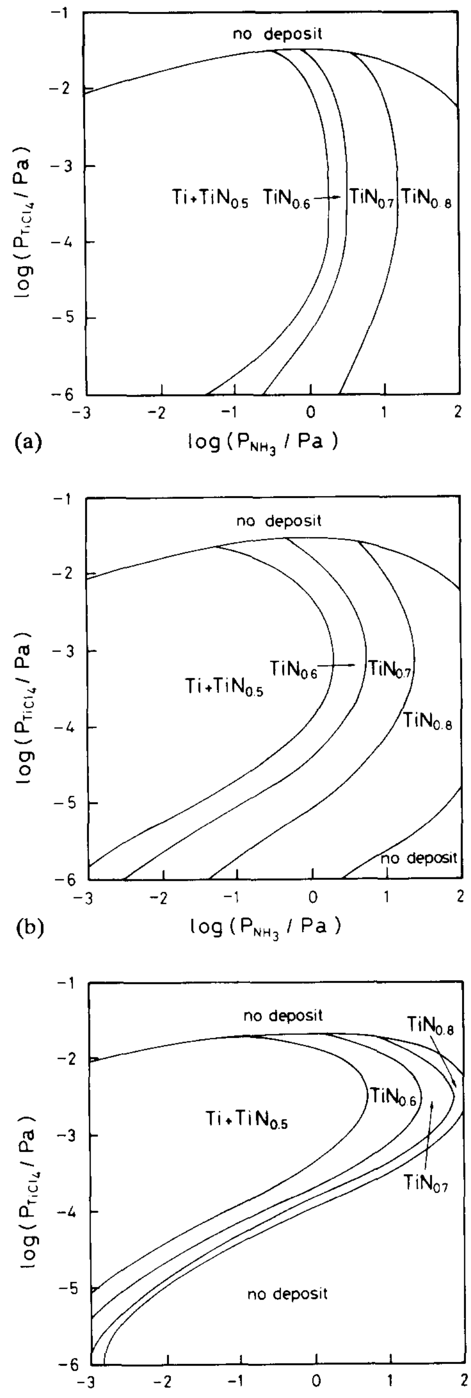

Fig. 3. The deposition domains of non-stoichiometric TiN$_x$ calculated as a function of the input composition, *i.e.* TiCl$_4$ and NH$_3$ partial pressures: (a) 1373 K; (b) 1573 K; (c) 1873 K.

Fig. 4) may suggest that the formation of intermediate species (such as imides or amides) in the gas phase could be an important process for the deposition of the non-stoichiometric TiN$_x$ plates.

Figure 5 shows the relationship between the density and the nitrogen-to-titanium atomic ratio of CVD TiN$_x$ plates. The density increased from 5.1 to 5.4×10^3 kg m^{-3} on increasing x from 0.74 to 1.0. The theoretical densities calculated from the lattice parameters and the compositions are in agreement with the experimental densities. This means that the CVD TiN$_x$ plates prepared in the present work are highly dense and pore-free deposits.

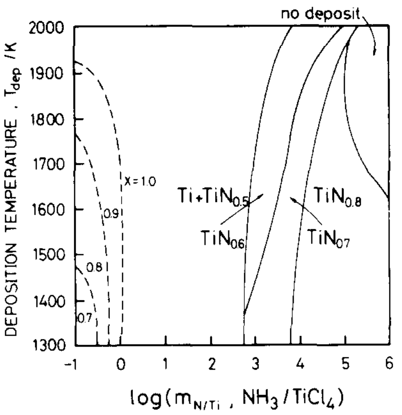

Fig. 4. Comparison of the calculations with the experimentally obtained deposition domains of non-stoichiometric TiN$_x$.

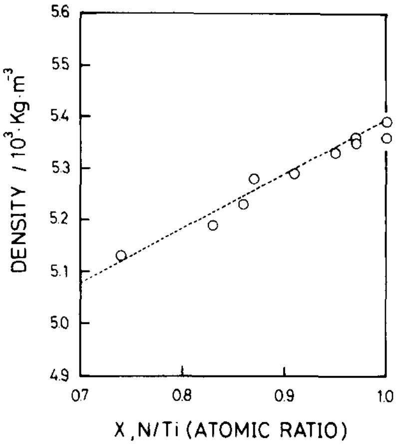

Fig. 5. Relationship between the density and the nitrogen-to-titanium atomic ratio of CVD TiN$_x$ plates: ○, experiments; – – – –, calculated density.

Figure 6 depicts the relationship between the lattice parameter and the nitrogen-to-titanium atomic ratio of CVD TiN$_x$ plates. The lattice parameters varied from 0.4228 to 0.4240 nm on increasing x from 0.74 to 1.0. Figure 7 summarizes the lattice parameters and compositions (nitrogen-to-titanium atomic ratios) for several kinds of non-stoichiometric TiN$_x$ reported in the past [9–15]. The relationship between the lattice parameter and the composition obtained in the present work is in good agreement with those of high purity samples prepared by nitriding pure titanium metals [9, 10] and by CVD from the TiCl$_4$–N$_2$–H$_2$ system [11, 12]. Figure 7 suggests that TiN$_x$ films prepared by physical vapour deposition (PVD) [12–15] may have larger lattice pa-

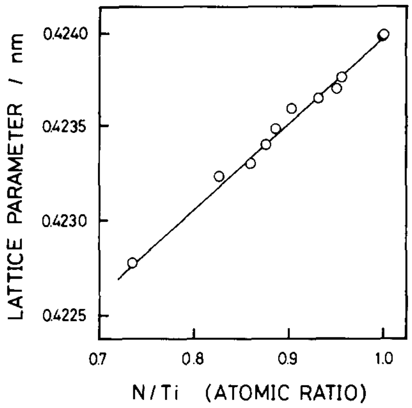

Fig. 6. Relationship between the lattice parameter and the nitrogen-to-titanium atomic ratio of CVD TiN_x plates.

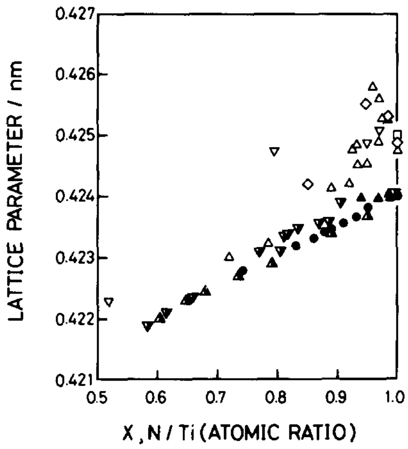

Fig. 7. Lattice parameters and compositions (nitrogen-to-titanium atomic ratios) of non-stoichiometric TiN_x: ▴, nitrided titanium metal [9]; ▾, nitrided titanium metal [10]; ▲, CVD TiN_x [11]; ■, CVD TiN_x [12]; ●, CVD TiN_x (present work); □, PVD TiN_x [12]; ◇, PVD TiN_x [13]; △, PVD TiN_x [14]; ▽ PVD TiN_x [15].

rameters than those obtained by CVD or nitriding titanium metals.

It is known that PVD films could contain extremely large internal stress partly because inert gases such as argon are involved in the films. For example, internal stresses of about several 1000 MPa were observed in PVD TiC films deposited on molybdenum substrates [16]. Wolfe *et al.* [12] reported that the lattice parameters of CVD and PVD $TiN_{1.0}$ films were 0.4240 nm and 0.4250 nm respectively. They explained that the reason for the difference could be internal stress. Sundgren *et al.* [14] reported that sputtered TiN_x films had larger lattice parameters than bulk materials did, which was caused by internal stress. Oxygen impurities may also increase the lattice parameter, as in the case of TiC_x [17]. In the present work, the oxygen impurity content was almost below the sensitivity of EPMA (approximately 0.04 wt.%). The lattice parameters of the CVD TiN_x plates obtained in the present work were the lowest of the previously reported results. This possibly means that the CVD TiN_x plates may have a very low level of impurities and internal stress.

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