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Growth of TiN films at low temperature

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Abstract

Thermodynamic analysis on growth of TiN films was given. The driving force for deposition of TiN is dependent on original Ti(g)/N(g) ratio and original partial pressure of N(g). TiN films were deposited by ion beam assisted electron beam evaporation system under suitable nitrogen gas flow rate at 523 K while the density of plasma varied with diverse discharge pressure had been investigated by the Langmuir probe. TiN films were characterized by means of Fourier transform infrared absorption spectrum (FTIR), X-ray diffraction (XRD) and observed by means of atom force microscopy (AFM). The results of these measurements indicated preferential TiN(1 1 1) films were deposited on substrate of Si(1 0 0) and glass by ion beam assisted electron beam evaporation system at low temperature, and it was possible for the deposition of TiN films with a preferential orientation or more orientations if the nitrogen gas flow rate increased enough. Sand Box was used to characterize the fractal dimension of surface of TiN films. The results showed the fractal dimension was a little more than 1.7, which accorded with the model of diffusion limited aggregation (DLA), and the fractal dimension of TiN films increased with increase of the temperature of deposition.

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Keywords: Titanium nitride (TiN); Driving force; Fractal dimension; Temperature of deposition

1. Introduction

Titanium nitride (TiN) is a promising material for many excellent properties, such as its high hardness, high melting temperature, high thermal and electrical conductivity, and good resistance to corrosion, abrasion, and oxidation. These properties of TiN are extremely important in a wide range of technological applications [1–3].

TiN films have been studied intensively for some years. The information on TiN films deposited under high temperature is available in many literatures [4–8]. Pihosh et al. got TiN films by rf magnetron sputtering below 1073 K [9]. Gerlach et al. obtained TiN films by reactive evaporation at 1023 K [10]. Kodanbaka et al. got TiN films by dc magnetron sputtering at 1030 K [11]. Patsalas et al. obtained TiN films by reactive magnetron sputtering [12]. But there are few reports on TiN films deposited under temperature which was lower than 673 K, and there are few reports on thermodynamic analysis on growth of TiN films, and TiN films are scarcely deposited by electron beam evaporation system.

Since Mandelbrot brought forward the theory of fractal [13], it was known that the fractal dimension could be used to describe complex coarse surface. Meakino believed that the surface of film far from equilibrium was a kind of self-similar fractal structure and could be described with the fractal dimension [14].

2. Thermodynamic analysis on growth of TiN films

In our system, we divided the process of growth of TiN films into following stages:

(1) Mixed gas and excited particles were delivered to the deposition area;
(2) Reactant molecules that remained gas phase were diffused onto substrate surfaces;
(3) Chemical reactions occurred between absorbed molecules or between absorbed molecules and gas molecules, at the same time desired deposition particles migrated on substrate surface and combined into crystal lattice.

From the phase diagram of N–Ti system, we know there can be two reaction as following near the vapor–solid interface when

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temperature is lower than 3223 K.

$$\mathrm{Ti(g)} + \mathrm{N(g)} \rightarrow \mathrm{TiN(s)} \tag{1}$$

$$2\mathrm{Ti(g)} + \mathrm{N(g)} \rightarrow \mathrm{Ti_2N(s)} \tag{2}$$

Here, g and s denote gas phase and solid phase.

The region of Ti_2N in the phase diagram of N–Ti system is much less than that of the region of TiN. In order to simplify the model, we assume that reaction (1) is the dominant reaction to be discussed in this study. The equilibrium constant expression of reaction (1) is:

$$K_{\mathrm{P}} = \frac{1}{P_{\mathrm{Ti}} P_{\mathrm{N}}} \tag{3}$$

The following limitation can be obtained from reaction (1).

$$P_{\mathrm{N}}^0 - P_{\mathrm{N}} = P_{\mathrm{Ti}}^0 - P_{\mathrm{Ti}} \tag{4}$$

Here, P_{N}^0 and P_{Ti}^0 denote original partial pressure of corresponding element respectively, P_{N} and P_{Ti} denote equilibrium partial pressure of corresponding element respectively. The driving force of reaction (1) can be obtained from expression (3) and (4):

$$\begin{aligned}\Delta P &= P_{\mathrm{N}}^0 - P_{\mathrm{N}} = P_{\mathrm{N}}^0 - \frac{P_{\mathrm{N}}^0(1-x) + \sqrt{P_{\mathrm{N}}^0(1-x^2) + 4/K_{\mathrm{P}}}}{2} \\ &= \frac{P_{\mathrm{N}}^0}{2}\left(1 + x - \sqrt{(1-x)^2 + \frac{4}{K_{\mathrm{P}} P_{\mathrm{N}}^{02}}}\right)\end{aligned} \tag{5}$$

Here, $x = P_{\mathrm{Ti}}^0 / P_{\mathrm{N}}^0$, denotes original Ti(g)/N(g) ratio. The equilibrium constant of reaction (1) is the following expression:

$$\Delta G^0 = -RT \ln K_{\mathrm{P}} \tag{6}$$

We can obtained ΔG^0 from the following expression [15,16]:

$$\Delta G^0 = A + BT \ln T + CT + DT^2 \tag{7}$$

Here, $A = -83{,}750$, $B = -11.91$, $C = 123.7$, $D = -4.7 \times 10^{-4}$.

Fig. 1 shows the driving force for deposition of TiN, ΔP, which is as a function of original Ti(g)/N(g) ratio for several original partial pressure of N(g) at 523 K. The driving force depends on original Ti(g)/N(g) ratio and original partial pressure of N(g) which is influenced by a nitrogen gas flow rate indirectly in our system. ΔP decrease with the decrease of P_{N}^0, and we can see that the value of ΔP will be very low if the value of P_{N}^0 is too low. So, TiN films can't be deposited easily unless the value of P_{N}^0 is high enough. As shown in Fig. 1, when P_{N}^0 remains constant, ΔP will increase with the increase of original Ti(g)/N(g) ratio up to some value, then it becomes constant too.

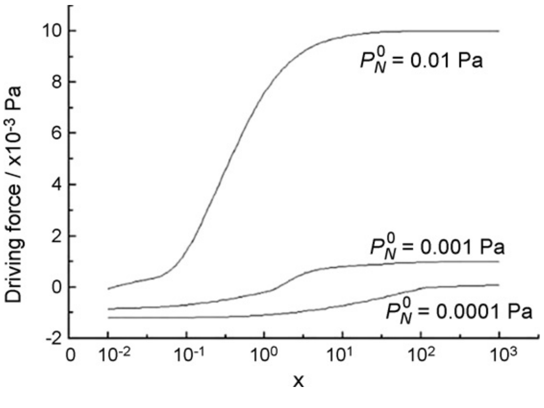

Fig. 1. The driving force for deposition of TiN, ΔP, which is as a function of original Ti(g)/N(g) ratio for several original partial pressure of N(g) at 523 K.

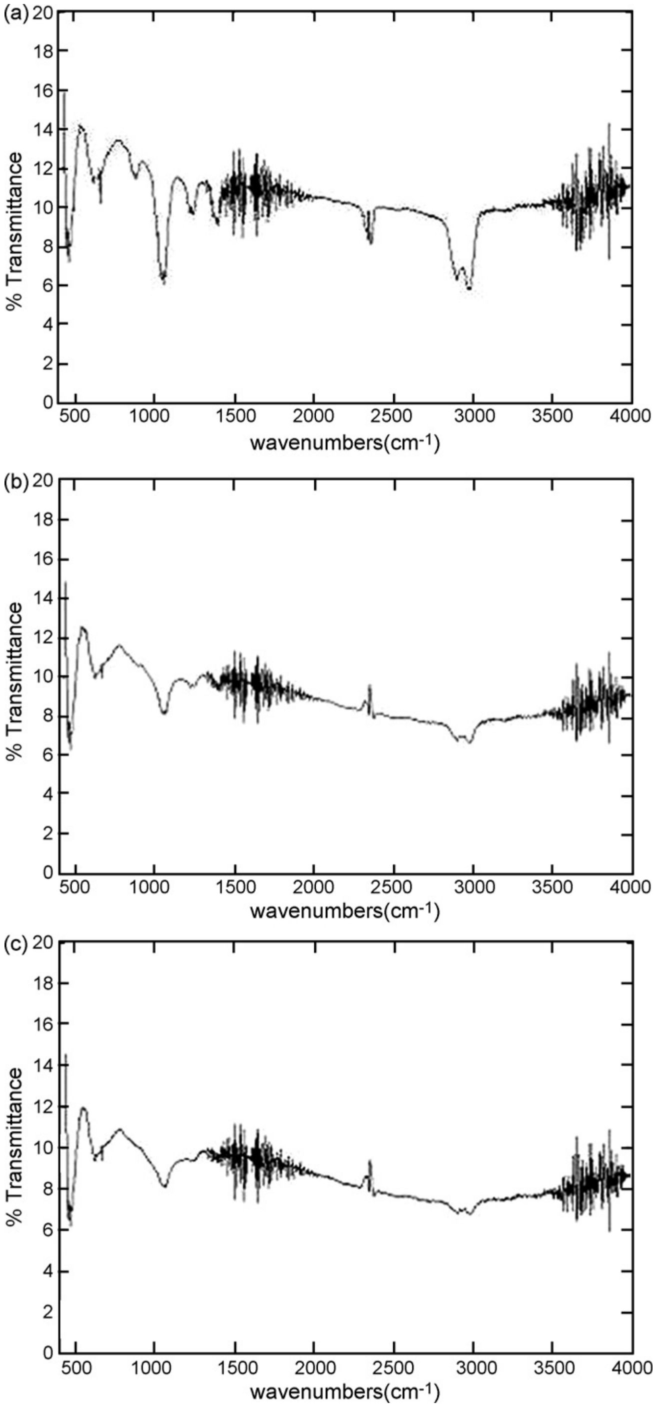

Fig. 2. The FTIR spectra of deposited TiN films on glass under diverse nitrogen gas flow rate. (a) 1#: 31.1; (b) 2#: 37.7; (c) 3#: 41.2.