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Author(s)	Shimozuma, M.; Date, H.; Iwasaki, T.; Tagashira, H.; Yoshino, M.; Yoshida, K.
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Three-dimensional deposition of TiN film using low frequency (50 Hz) plasma chemical vapor deposition

M. Shimozuma[a] and H. Date
College of Medical Technology, Hokkaido University, Sapporo 060, Japan

T. Iwasaki and H. Tagashira
Department of Electrical Engineering, Hokkaido University, Sapporo 060, Japan

M. Yoshino
Hokkaido Polytechnic College, Zenibako 3-190, Otaru 047-02, Japan

K. Yoshida
Department of Electrical and Electronic Engineering, Kitami Institute of Technology, Kitami 090, Japan

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Titanium nitride (TiN) films have been deposited on three-dimensional substrates by low frequency (50 Hz) plasma chemical vapor deposition method using a $TiCl_4+N_2+H_2$ mixture at a substrate temperature of 550 °C with a substrate bias circuit using two diodes. The maximum value of the deposition rate was 1200 nm/h at a substrate bias voltage V_B of −150 V and the ratio of flow rate $k(N_2/TiCl_4)=2$. The maximum value of Vickers hardness of deposited TiN films using Micro–Vickers hardness tester was about 2400 Hv at $k=2$ and $V_B=-150$ V bias voltage. There were practically no differences between the deposition rates and Vickers hardness on vertical and horizontal substrate surfaces against the surface of electrodes. Resistivity of the films was about 80 $\mu\Omega$ cm at V_B from 40 to −150 V with $k=2$. However, the hardness of deposited film with no substrate bias was about 1000 Hv. This demonstrates the importance of the substrate bias to make uniform and high quality film deposition on three-dimensional substrate surfaces by setting the substrate in the middle of the interelectrode gap. The composition of deposited TiN films was measured by Auger spectra method. It was found that Ti, N, Cl, O, and C were contained in the deposited TiN films. The at. % value of the Cl content [=Cl/(Ti+N+O+C+Cl)] in the TiN films was about 2% with substrate bias voltage, and the ratio of N/Ti was about 1.2. [S0734-2101(97)00904-4]

I. INTRODUCTION

Titanium nitride (TiN) is a material having the properties of high surface hardness, good wear resistance, good corrosion resistance, low friction coefficient, high electrical conductivity, and golden color. For these material properties, the TiN films are widely used in the field of many industries, such as cutting tool surface hardening,[1] personal ornaments coating, diffusion barrier layer in semiconductor devices,[2] and biomedical materials.[3] Therefore, it is necessary to investigate the techniques to deposit TiN film on objects in various shapes. In general, TiN films are deposited by thermal and plasma chemical vapor deposition (CVD) physical vapor deposition, (PVD) and plasma spraying methods. However, the PVD and plasma spraying are not appropriate to deposition of TiN film on the three-dimensional objects because of nonuniformity and poor step coverage on objects in complex shapes.[4] The plasma CVD offers good uniformity of TiN film on objects in various shapes.

This article reports the deposition of golden color high quality TiN films on the three-dimensional substrate at 550 °C by the 50 Hz plasma CVD[5,6] with substrate bias method using $TiCl_4+N_2+H_2$ mixture. Maximum deposition rate, Vickers hardness, and resistivity of deposited TiN films were 1200 nm/h, 2300 Hv, and 80 $\mu\Omega$ cm, respectively. The at. % value of the Cl content [=Cl/(Ti+N+O+C+Cl)] in the TiN films was about 2%, and N/Ti ratio was about 1.2. Moreover, the Vickers hardness and the deposition rate of the deposited films on every surface of the three-dimensional substrate were almost equal. Accordingly, it was found that the 50 Hz plasma CVD with a bias circuit using two diodes is a suitable method for the three-dimensional deposition.

II. EXPERIMENT

The experimental apparatus is similar to that of Ref. 7 and shown schematically in Fig. 1. Briefly, the plasma reactor was evacuated by a diffusion pump backed by a rotary pump. The steel plasma reactor is 40 cm in diameter and 60 cm in height. The electrodes were made of 10-cm-diam stainless steel with 5 cm gap between the two electrodes. The 50 Hz power is supplied at the upper electrode, and the lower is grounded. The stainless steel rod built in the heater to heat the three-dimensional stainless steel substrate (14 mm×14 mm×20 mm) is inserted into the middle of the interelectrode gap. The rod is insulated electrically from the grounded reactor. Accordingly, it is electrically biased with respect to the two electrode potential every half cycle using two diodes for the three-dimensional deposition. The excited 50 Hz plasma between the upper and lower electrodes with

[a]Electronic mail: smzm@cme.hokudai.ac.jp

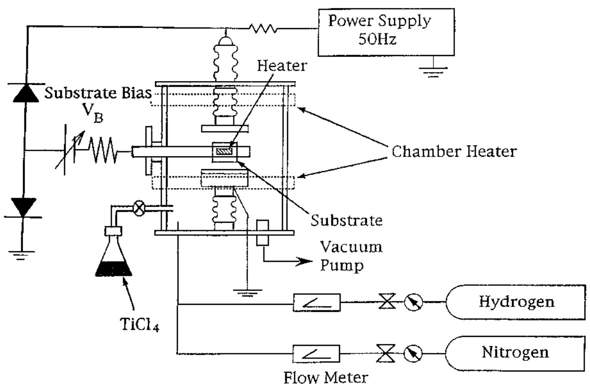


FIG. 1. Schematic diagram of the plasma CVD apparatus with substrate bias circuit using two diodes.

the bias circuit was symmetrical with regard to the rod heater, and the potential of the rod heater, on which the substrate was attached, was always lower than that of both electrodes. Applied voltage and plasma photoemission waves between two electrodes and the substrate with -50 V bias voltage are shown in Fig. 2. It was found that the two plasmas between the two electrodes and the substrate are excited alternately by the bias circuit. Various potentials can be applied to the substrate by the bias circuit with two diodes, and bombarding positive ion energy to the three-dimensional substrate is controlled by the substrate bias potential. The

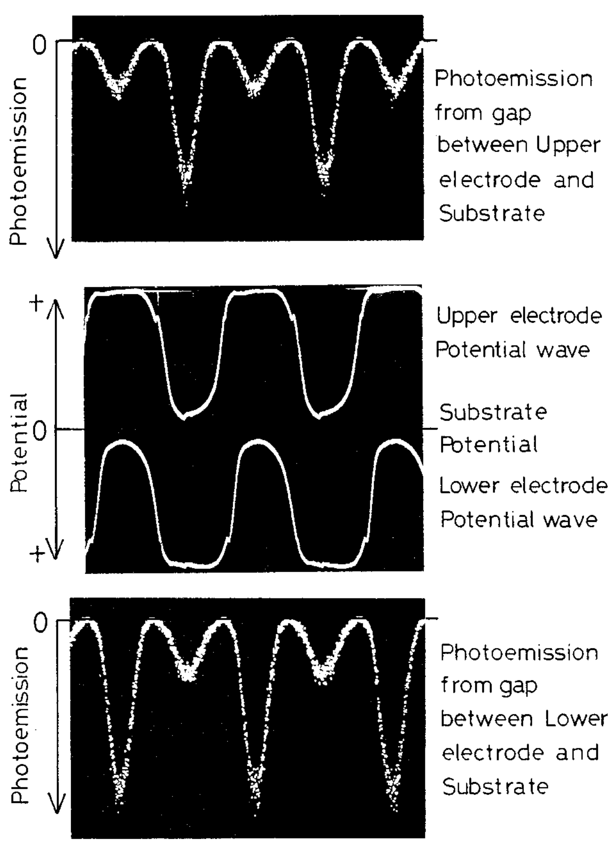


FIG. 2. Applied voltage and plasma photoemission waves between two electrodes and substrate.

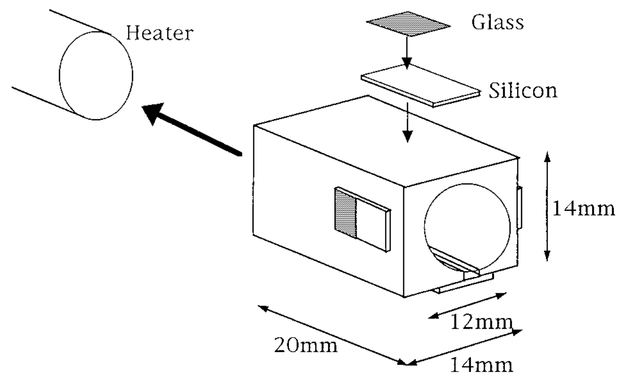


FIG. 3. Schematic diagram of three-dimensional substrate.

effect of the ion bombardment cannot be disregarded. It seems that the kinetic energy of the bombarding ion is consumed as migration energy for rearrangement of deposited atoms, resulting in the deposition of high quality films. The temperature of the rod heater is measured by the thermocouple in the rod heater. Silicon tips were set on the four surfaces of the stainless steel substrate as shown in Fig. 3. Vickers hardness, the deposition rate, resistivity, and the composition of the deposited TiN films on these silicon tips were measured. The gases used in the experiment were $TiCl_4$, N_2, and H_2. These gases were introduced in the reactor at a rate of 10, 10–40, and 400 sccm, respectively. The substrate temperature was 550 °C constantly throughout the entire course of the work. Conditions for deposition of TiN film in this work are listed in Table I. Resistivity of deposited TiN films was measured by a four-point probe method. The deposited TiN film composition was measured by the Auger spectra method. Photoemission intensity from the plasma was observed by monocromator and photomultiplier.

III. RESULTS AND DISCUSSION

A. Deposition rate of TiN film

Figure 4 shows the dependence of the deposition rate of the TiN film on the ratio of flow rate $k = N_2/TiCl_4$ with constant $TiCl_4$ and H_2 flow rates (10 and 400 sccm, respectively) and substrate bias voltage $V_B = -100$ V. The deposition rate of TiN film increases with increasing k until it reaches the maximum value of about 1100 nm/h at $k = 2.0$, and then it decreases. The dependence is similar to the rf plasma CVD result.[8] The deposition rate of all the faces is almost equal, that is, uniform TiN films are deposited on the three-

TABLE I. Deposition condition.

Power frequency		50 Hz
Plasma current		200 mA
Gap length		5 cm
Pressure		1 Torr
Substrate temperature		550 °C
Gas flow	$TiCl_4$	10 sccm
	N_2	10–40 sccm
	H_2	400 sccm
Bias V_B		40 to -200 V
Substrate		Stainless steel (14 mm×14 mm×20 mm) Silicon tip

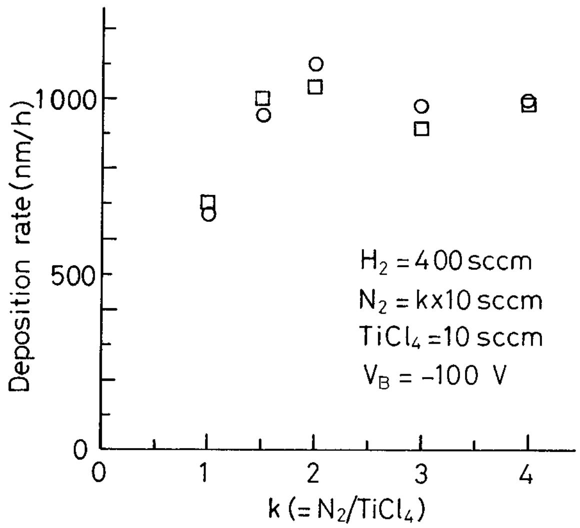


FIG. 4. Dependence of the deposition rate on the ratio of flow rate k ($=N_2/TiCl_4$). (□) Perpendicular faces to the electrodes, (○) parallel faces to the electrodes.

dimensional substrate. Figure 5 shows the deposition rate against the substrate bias voltage with $k=2$. This curve was found to have a maximum value at about $V_B=-150$ V. The maximum value of deposition rate was about 1200 nm/h. The deposition rate increased with increasing negative bias voltage, and then it decreased. From the results of observed photoemission waves in Fig. 6, it was found that the continuous plasma was excited by the applied negative bias potential -200 V to the substrate, in spite of the 50 Hz plasma power frequency. This shows that the charged species in the plasmas between the two electrodes and the substrate were accelerated with increasing negative bias V_B, and the deposition rate increases with V_B. Moreover, increasing negative bias, it seems that deposited film is etched by many high energy positive ions. It appears that the deposition rate of the

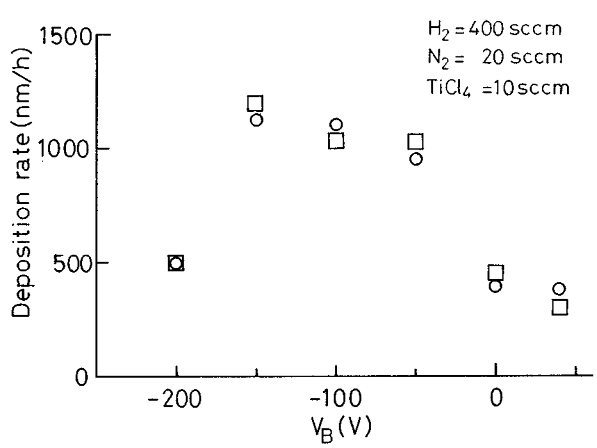


FIG. 5. Dependence of the deposition rate on substrate bias potential (V_B). (□) Perpendicular faces to the electrodes, (○) parallel faces to the electrodes.

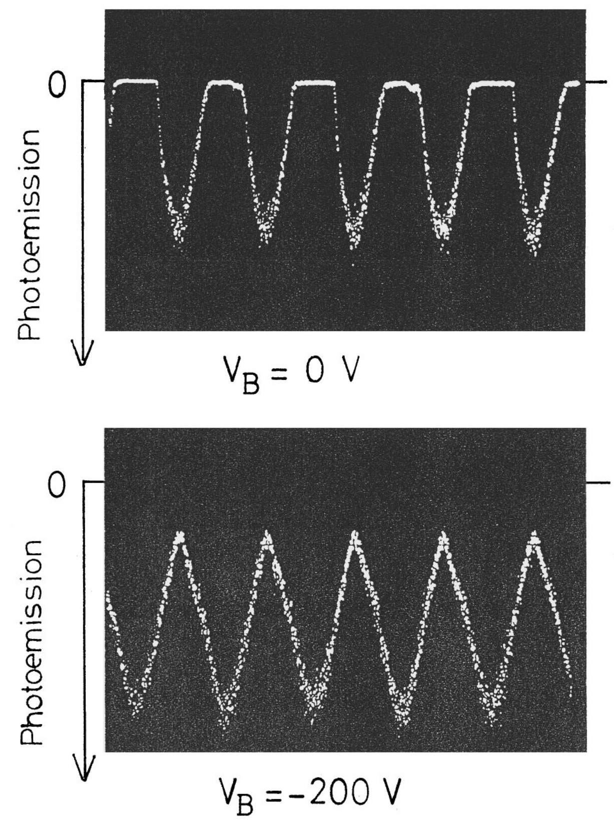


FIG. 6. Plasma photoemission waves near the substrate at substrate bias $V_B=0$ and -200 V.

vertical substrate surface against the surface of the electrodes agrees with that of horizontal surface substrate from Figs. 4 and 5.

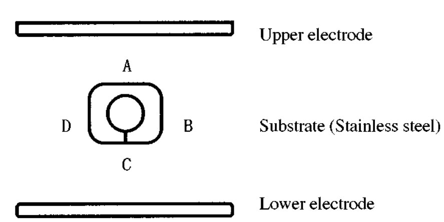
B. Vickers hardness of TiN film

Figure 7 shows the dependence of Vickers hardness of TiN film on the gas flow rates ratio k. Vickers hardness is more than 2000 Hv at $1<k<3$ with $V_B=-100$ V. The highest value of Vickers hardness is about 2400 Hv at $k=2$. Moreover, Vickers hardness of all the faces are almost

TABLE II. Three-dimensional deposition result.

Substrate surface	A	B	C	D
Deposition rate (nm/h)	1100	1100	1000	1030
Vickers hardness (Hv)	2294	2292	2383	2320

Deposition condition
H_2:400 sccm, N_2:20 sccm, $TiCl_4$:10 sccm,
T:550 °C, V_B: -100 V, P:1.1 Torr



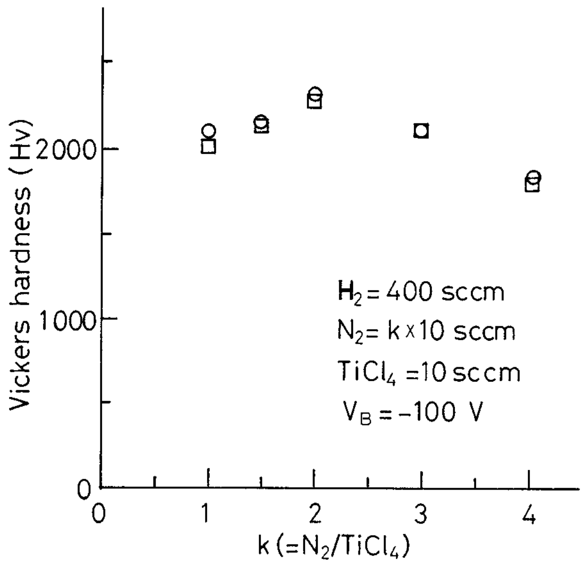


FIG. 7. Dependence of the Vickers hardness on the ratio of flow rate k ($=N_2/TiCl_4$). (□) Perpendicular faces to the electrodes, (○) parallel faces to the electrodes.

equal. The Vickers hardness of deposited TiN films was measured by a micro-Vickers hardness tester with a load of 2–5 gf. The Vickers hardness of the deposited films is above 2000 Hv using the negative bias circuit with two diodes. However, the hardness of deposited films without substrate bias circuit (substrate has floating potential) was about 1000 Hv. From Fig. 8, the Vickers hardness of the deposited film keeps nearly constant value in the range of $40>V_B>-200$ V, because the substrate potential is always lower than that of both (upper and lower) electrodes with every half cycle for using the bias circuit. The Vickers hardness and the deposition rate of each surface on the substrate were shown in Table II, and there is no difference in values of the hardness and the deposition rate against each surface.

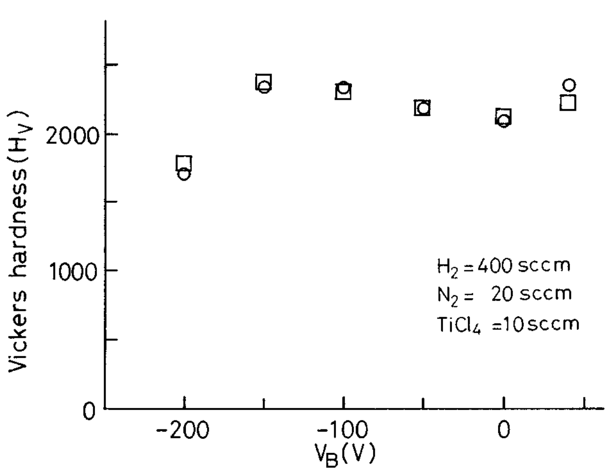


FIG. 8. Dependence of the Vickers hardness on substrate bias potential (V_B). (□) Perpendicular faces to the electrodes, (○) parallel faces to the electrodes.

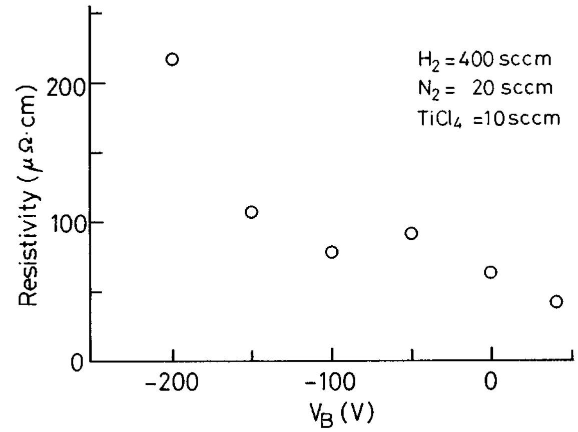


FIG. 9. Resistivity against V_B of deposited TiN film.

C. Resistivity of TiN film

Resistivity against V_B of the deposited TiN films at $k=2$ is shown in Fig. 9. Values of deposited TiN resistivity were about 80 $\mu\Omega$ cm in a range of $40>V_B>-150$ V, but the resistivity was about 220 $\mu\Omega$ cm at $V_B=-200$ V. It seems that the deposited film was broken down by bombardment of many high energy positive ions, and, as seen in the scanning electron microscope (SEM) photograph, the deposited film has a rough surface.

D. TiN film composition and N/Ti ratio

In Fig. 10, the deposited TiN film's composition from Auger spectra is shown. It was found that Ti, N, Cl, O, and C were contained in the deposited TiN films. It appears that these composition values of deposited TiN films have constant values against V_B, in Fig. 10. The at. % value of the Cl content $[=Cl/(Ti+N+O+C+Cl)]$ in the TiN films is about 2% in the range of $40>V_B>-200$ V bias potential. The C content was about 10% because an oil rotary pump and an oil diffusion pump were used in the vacuum system. The ratio of

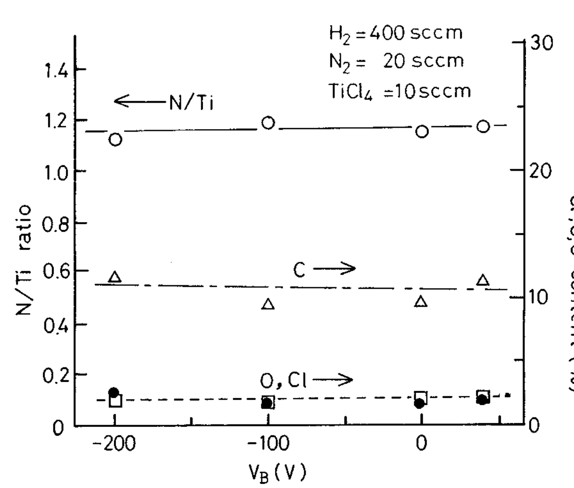


FIG. 10. The deposited TiN films' composition and N/Ti ratio as a function of V_B. (○) N/Ti ratio, (△) C content, (●) Cl content, and (□) O content.

N/Ti was about 1.2. The deposited TiN film has a light golden color in a range of $40 > V_B > -200$ V.

From these results, it was found that high quality and uniform TiN film deposition on three-dimensional substrate surface was performed by the bias deposition condition and substrate set in the middle of the interelectrode gap.

IV. CONCLUSIONS

Golden color high quality TiN films have been deposited on the three-dimensional substrate at 550 °C by the 50 Hz plasma CVD with the substrate bias method using $TiCl_4 + N_2 + H_2$ gas mixtures. Maximum deposition rate, Vickers hardness, and resistivity of deposited TiN films were 1200 nm/h, 2300 Hv and 80 $\mu\Omega$ cm, respectively, at the bias potential $V_B = -100$ V. The at. % value of the Cl content [=Cl/(Ti+N+O+C+Cl)] in the TiN films was about 2%, and N/Ti ratio was about 1.2. Moreover, the Vickers hardness and the deposition rate of deposited films on every surface of the three-dimensional substrate were almost equal. Accordingly, it was found that high quality and uniform TiN film deposition on three-dimensional substrate surface was performed by using a bias circuit with two diodes and the substrate set in the middle of the interelectrode gap.

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