SELECTIVE CONTROL OF PARTICLES BY ELECTRON-BEAM-EXCITED PLASMA AND ITS APPLICATION

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In EBEP (Electron-Beam-Excited Plasma) apparatus, the electron energy distribution is controlled easily by discharge current I_D and accelerating voltage V_A. As an application, TiN films are deposited, and the spectroscopic and Q-Mass measurement are promoted to reveal the deposition mechanism. The results are summarized as follows; (1) The film composition was identified with TiN and Ti_2N, and the ratio of [TiN]/[Ti_2N] increased with V_A whereas it was almost constant for I_D variation. (2) As for thickness, It increased with I_D and V_A. (3) From spectroscopic and Q-Mass measurement, number density and energy distribution of particles are controlled by I_D and V_A, respectively.

1. INTRODUCTION

In recent years, plasma of low electron and ion temperatures and high density is required in plasma process. EBEP is one of the apparatuses for production of such plasma[1][2]. The authors try to deposit a variety of thin films by using this apparatus. As the requirements of abilities have risen for optical device, electronic parts, memory device, energy device, etc., it has become important purpose for research workers to make them quality up and functional up. In general, the techniques utilizing ion are adopted for that purpose, and the film quality is known to depend on ion energy. EBEP suits for the techniques since electron density and energy are controlled easily in the plasma production with collision of electron against reactive ambient gas particles. In this paper, TiN film is deposited as an instance. The characters of TiN material are known to be excellent wear resistance, corrosion resistance, high thermal conductivity, high melting point, and high hardness[3]. Therefore, It is applied to a cutting tool and machine parts[4][5]. The application as a diffusion barrier in the ULSI (Ultra Large Scale Integrated circuit) process[6] also has been investigated. Moreover, TiN also possesses the golden color, so that it is used as ornament[7]. This useful film has been deposited by various techniques, for instance, sputtering[8], CVD (Chemical Vapor Deposition)[9], and PVD (Physical Vapor Deposition)[10]. In this experiment, ARE (Activated Reactive Evaporation) method which is a kind of PVD is adopted. In addition, the spectroscopic and Q−Mass measurements are also carried out to reveal the deposition mechanism.

2. EBEP APPARATUS AND EXPERIMENTAL CONDITIONS

The details of EBEP apparatus is shown in other papers[1][2]. It is made of pyrex glass, and divided into three regions by electrodes; one is discharge region to produce the plasma which is source of electron−beam, another is electron accelerating region to accelerate and extract high dense electrons, and the other is EBEP region to produce the processing plasma with the collisions of high−velocity electrons against particles of ambient gas. The plasma conditions are controlled easily by discharge current (I_D) and accelerating voltage (V_A).

Fig.1 shows only EBEP region applied as ARE apparatus and optical system. N_2 gas was introduced to EBEP region from another inlet and then the pressure was set at 7×10^{-4} Torr. The axial magnetic field at magnitude 80mT was applied in order to suppress the diffusion of beam−plasma to the wall, consequently N_2 plasma shaped into a beam of 1cm ϕ was produced.

The substrates and Ti evaporator were placed as shown in the figure. Alumina (Al_2O_3), quartz (SiO_2), and silicon (Si(111)) of 1cm square were employed as substrates. Metal evaporation is caused by electron−beam in ordinary ARE, but by ion in this experiment because it is reported that ion current in this apparatus is very high[1]. When the negative voltage V_E is applied to the Ti evaporator, the ions in plasma are accelerated to the evaporator and heat it up. The Ti atoms react with the N_2 plasma, and deposit as film on the substrate surface. TiN films were deposited as functions of I_D (3, 4, and 5A) and V_A (80, 90, and 100V). The

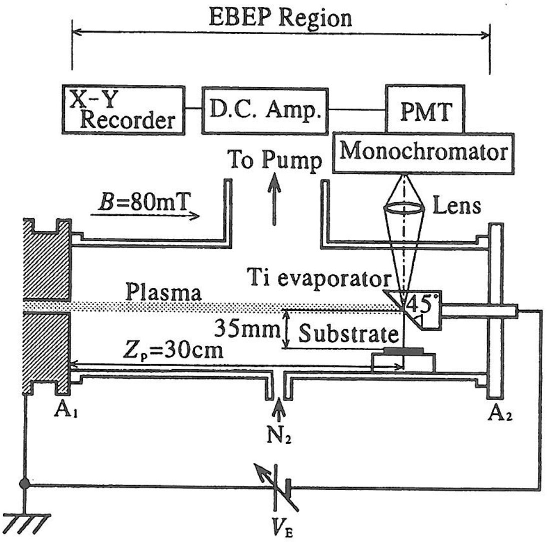

Fig.1. Deposition apparatus and optical system.

deposition time was kept constant at 1 hour. The dependence of Mass spectrum and of radiation spectra on V_A and I_D were measured. The range of wave length measured was from 350 to 500nm.

3. CONTROL OF TiN FILM DEPOSITION

Color of film deposited changed for V_A variation whereas it changed little for I_D regardless of substrate materials. The change of film color for V_A is shown in table 1. The color for 80V is yellowish gold, and it becomes gold according as V_A increases. The chemical compound film between Ti and N is known to change its color for its composite ratio[11][12]. According as ratio of [Ti]/[N] approaches 1, the color becomes gold. Therefore, it is expected that the composition is

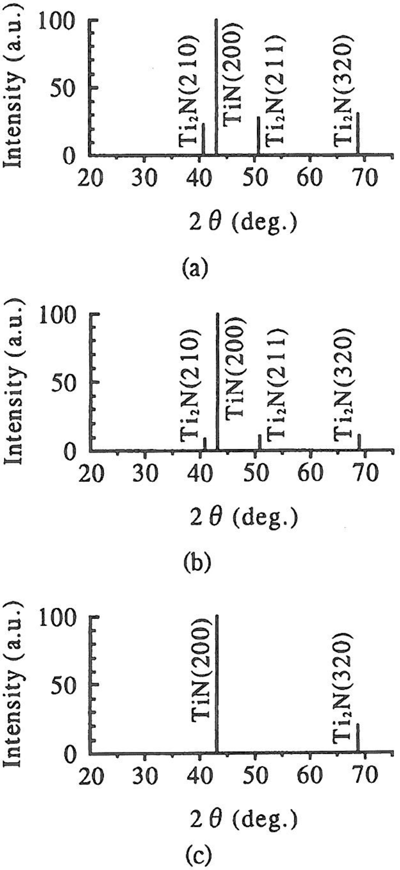

Fig.2. X−ray diffraction pattern. (V_A: 100V, Deposition time: 1 hour, Substrate: Si); (a) I_D=3A, (b) 4A and (c) 5A

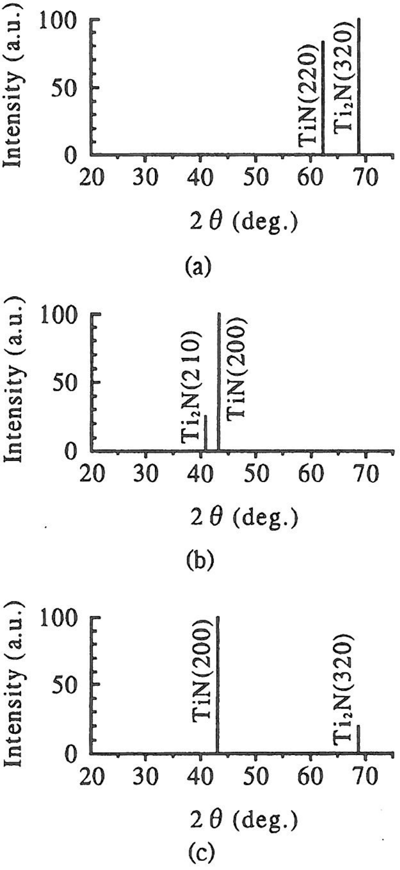

Fig.3. X−ray diffraction pattern. (I_D: 5A, Deposition time: 1 hour, Substrate: Si); (a) V_A=80V, (b) 90V and (c) 100V

Table 1. The Color of Films.

V_A (V)	Color
80	Yellowish gold
90	Reddish gold
100	Gold

Table 2. The Film Conductivity.

I_D (A) V_A (V)	3	4	5
80	5.60×10^4	3.35×10^4	
90	3.42×10^5	5.95×10^5	9.99×10^5
100	3.78×10^5	9.24×10^5	1.07×10^6

Unit: S/m

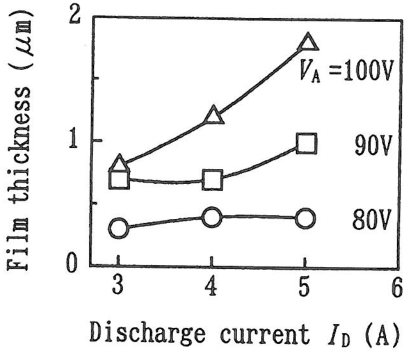

Fig.4. Film thickness. (Deposition Time: 1 hour, Substrate: Si)

controlled by V_A.

Composition of the films was identified with TiN and Ti_2N by using X−ray diffraction. Fig. 2 shows the diffraction pattern of film on Si substrate for I_D variation. The intensity ratio of TiN to Ti_2N peaks is almost constant for I_D, i.e. it shows that the film composition varies little. Fig. 3 shows the diffraction pattern for V_A variation similarly. The intensities of Ti_2N decrease as compared with those of TiN as V_A increases, i.e. the composition is controlled by V_A. These results accord with the change of the film color to gold.

Fig. 4 shows the thickness on Si substrate versus I_D for different V_A, which is measured by the surface roughness meter. It increases with I_D and V_A. This tendency is also same for the other substrates, and the thickness is ～2 μm regardless of substrate materials. Accordingly, deposition rate is controlled both by I_D and V_A. However, control of deposition rate by I_D is better than that by V_A because the composite ratio is able to be kept constant.

Electrical conductivity at 27 ℃ was measured by conductivity meter. Table 2 shows the values of the films deposited at different V_A and I_D on Si substrate. The values vary with V_A and I_D, and were $\sim10^6$ S/m regardless of substrate materials. The values for the films possessing gold color are the magnitude order of 10^5 S/m. This values are reasonable since the conductivity of TiN at room temperature is reported to be about 5×10^5 S/m[13][14].

4. DEPENDENCE OF SPECTRAL INTENSITIES BY SPECTROSCOPIC MEASUREMENT ON I_D AND V_A

N_2 2nd positive, N_2^+ 1st Negative and N^+ spectra were identified from the

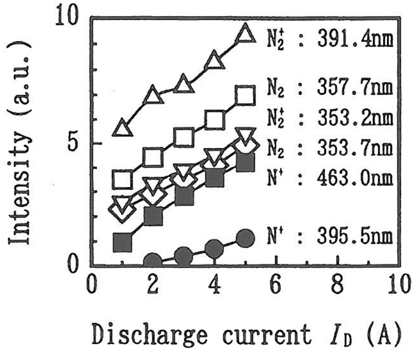

Fig.5. Dependence of spectral intensity on discharge current I_D. (V_A=100V)

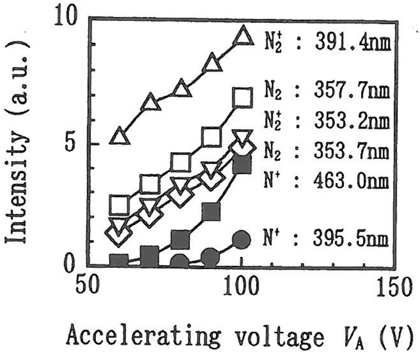

Fig.6. Dependence of spectral intensity on accelerating voltage V_A. (I_D=5A)

radiation. Fig. 5 shows the spectral intensities as a function of I_D. The intensities increase according as I_D increases. The ratios between the spectral intensities are almost constant for I_D variation[15]. It is indicated that energy distribution of electron does not change much, i.e. electron−beam density is controlled. Therefore, densities of excited molecules, atoms and ions are controlled by I_D since only electronic impact causes excitation and ionization under the experimental conditions.

Fig. 6 shows the intensities as a function of V_A. The intensities increase according as V_A increases. In particular, the intensity N^+ markedly increases as compared with the others. It is shown that N_2 dissociate markedly as V_A increases. It is indicated that particles energy is controlled by V_A. The similar results are obtained about Q−Mass measurement[16].

5. DISCUSSION

The measurement results for I_D variation are explained as follows; the number of particles excited and ionized in ambient gas is controlled by I_D without change of the energy distribution[15]. Thus, deposition rate is controllable in film deposition.

Those for V_A are explained as follows; energy of dissociation for N_2 due to electron impact is more than that of ionization[17], i.e. for low V_A, the electrons less than dissociation energy is most of all, and some of them rise up to more than the energy with V_A. Energy state of molecules, atoms and ions of nitrogen becomes higher according as V_A increases, so that they for higher V_A are easy to react with Ti atoms. Therefore, the formation of TiN becomes dominant than that of Ti_2N according as V_A increases. In fact, It is reported that beam energy applied to substrate controlled Ti_2N growth in titanium nitride films deposited by PVD process[18]. Accordingly, film properties are controllable in film deposition.

6. CONCLUSION

As one of the applications of EBEP apparatus, TiN film deposition was tried by means of ARE. In this paper, the relation between films deposited and important parameters I_D and V_A has been first revealed. Regardless of substrate materials, the results are as follows; (1) Film composition is identified with TiN and Ti_2N. (2) The composite ratio $[TiN]/[Ti_2N]$ increases with V_A whereas it is almost constant for I_D variation. (3) Film thickness increases with I_D without change of the composite ratio, and its maximum value is about 2 μ m. (4) The electrical conductivity is the magnitude order of 10^5 S/m. From these results, it is found that the composition of film deposited and deposition rate are controlled by V_A and I_D, respectively.

Furthermore, the spectra radiated from the plasma in EBEP apparatus were measured under N_2 gas ambient in order to understand the behavior of particles in plasma, varying electron−beam density and energy. It is indicated from the results that number density and energy distribution of particles are controlled by I_D and V_A, respectively. Therefore, it is explained that the deposition rate and the film properties in film deposition are controlled by I_D and V_A, respectively.

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