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Effect of Substrate Bias Voltage on the Properties of Hafnium Nitride Films Deposited by Radio Frequency Magnetron Sputtering Assisted by Inductive Coupled Nitrogen Plasma

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Hafnium nitride (HfN) thin films were deposited onto a silicon substrate by inductive coupled nitrogen plasma-assisted radio frequency magnetron sputtering. The films were prepared without intentional substrate heating and a substrate negative bias voltage ($-V_b$) was varied from -50 to -150 V to accelerate the effects of nitrogen ions (N^+) on the substrate. X-ray diffractometer patterns showed that the structure of the films was strongly affected by the negative substrate bias voltage, and thin film crystallization in the HfN (100) plane was observed under deposition conditions of -100 V_b (bias voltage). Atomic force microscopy results showed that surface roughness also varied significantly with substrate bias voltage. Films deposited under conditions of -150 V_b (bias voltage) exhibited higher hardness than other films.

Keywords: Hafnium nitride, Sputtering, Ion beam, Atomic force microscopy, Microstructure

1. INTRODUCTION

It has been proposed that transition metal-nitrides such as hafnium nitride (HfN) are promising candidates for hard-coated thin films [1] due to their high resistance to wear and oxidation. Chemical vapor deposition [2], reactive radio frequency (RF) sputtering [3] and activated reactive evaporation [4] are all methods that have been developed for the preparation of high quality HfN films.

Among these deposition methods, reactive magnetron sputtering is recommended as an efficient method for the synthesis of high-rate-deposited HfN films. In conventional reactive magnetron sputtering for HfN deposition, it is well known that the main parameters controlling the properties of the films are substrate temperature and reactive nitrogen gas partial pressure in a sputtering atmosphere [5].

In this study, HfN films were deposited without intentional substrate heating by a magnetron sputtering system assisted by inductive coupled plasma (ICP), and then the effects of negative substrate bias voltage (V_b) on the surface morphology, microstructure, and the micro-hardness of the films were investigated.

The structural changes in HfN films subject to intense nitrogen ion (N^+) bombardments were explored using high resolution

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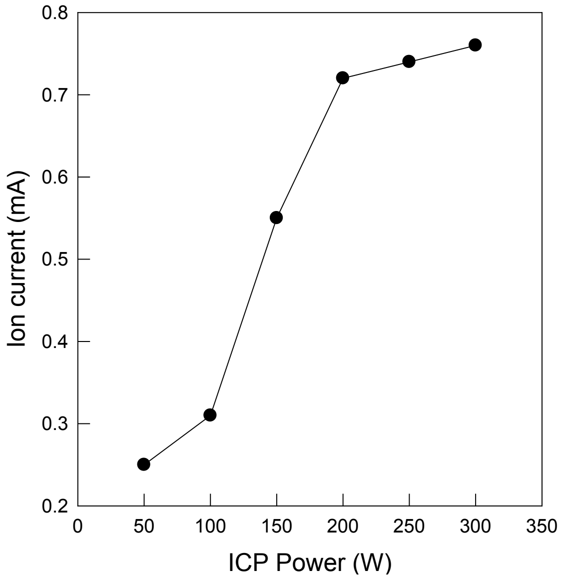

Fig. 1. Variation of the N^+ ionic current as a function of inductive coupled plasma (ICP) power applied on the antenna conductor.

X-ray diffractometer (XRD). The surface morphology and micro-hardness of the films were observed using an atomic force microscope (AFM) and a nano-indenter, respectively.

2. EXPERIMENTS

HfN films (300 nm thick) were deposited on a Si (100) substrate with an RF magnetron sputtering system assisted by inductive coupled nitrogen plasma. The antenna conductor, which was made of a Cu tube for water cooling, was located on the side wall of the chamber approximately 100 mm from the substrate. In order to produce N^+ ions, a three-turn antenna with a diameter of 200 mm was coupled to a RF power generator at 13.56 MHz via a matching network. The cylindrical quartz chamber for the N^+ ion source was 180 mm in diameter and 250 mm in length, and the N^+ ionic current as a function of ICP power applied to the antenna conductor was measured using a Faraday cup.

After the pressure in the chamber was lowered to 1×10^{-5} Pa, the HfN films were deposited from a pure Hf target (99.99%) with RF magnetron sputtering in pure argon (99.99% Ar) with N^+ ion beam assistance. The Ar and N_2 gas flow rates were kept constant at 10 sccm and 5 sccm, respectively. The substrate temperature was measured with a thermocouple in contact with the surface of the substrate.

Although deposition was carried out without intentional substrate heating, the substrate temperature increased up to 120°C due to the generation of plasma in the chamber. The Hf target power and the distance from the target to the substrate were kept constant at 120 W (power density: 4.5 W/cm^2) and 5 cm, respectively. During deposition, negative substrate bias voltages (-50, -100, -150 V_b) were applied to the substrate with a pulsed direct current power supply.

After deposition, composition of the films was evaluated using an auger electron spectroscopy (AES, MICROLAB 350; VG Scientific, Beverly, MA, USA) depth profile and the change in structure was characterized by XRD using Cu-Kα radiation at the Korea Basic Science Institute (KBSI, Daegu center). The surface morphology and root mean square (RMS) roughness were observed with AFM under atmospheric pressure.

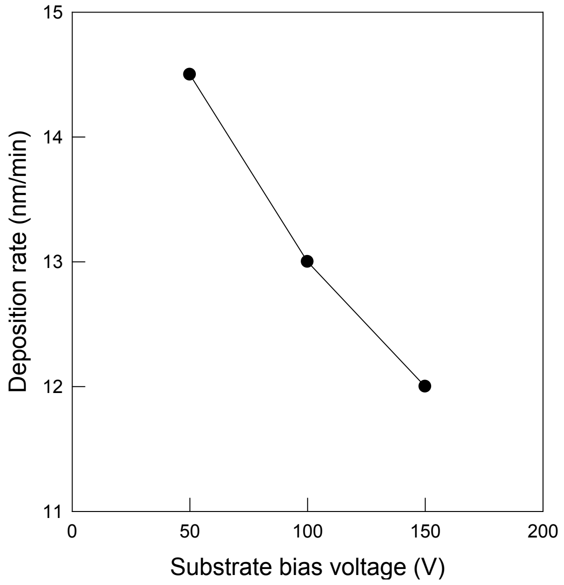

Fig. 2. Variation of deposition rate as a function of the negative bias voltage ($-V_b$).

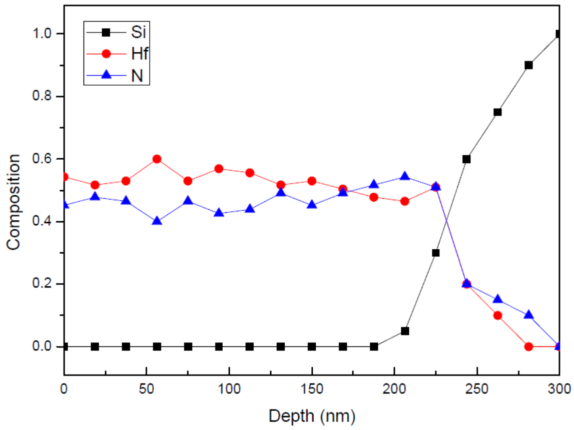

Fig. 3. Auger electron spectroscopy depth profiles of hafnium nitride (HfN) films deposited at -100 V_b.

3. RESULTS AND DISCUSSION

Figure 1 shows the N^+ ionic current, measured with a Faraday cup, as a function of ICP power applied on the antenna conductor. The measured current increased initially with ICP power and then the rate of increase declined above 200 W. The highest current was 0.76 mA at an ICP power of 250 W. In this study, the ICP power applied on the antenna conductor was set at 200 W.

When the deposition was carried out with a negative substrate bias ($-V_b$), the N^+ ions transferred their kinetic energy to the surface adatom on the substrate. Figure 2 shows the variation of deposition rate as a function of $-V_b$. As $-V_b$ increased, the deposition rate decreased from 15 (non-biased condition) to 12 nm (-150 V_b) per minute. Intense bombardment of N^+ ions may induce re-sputtering of the films [6], resulting in a decreased deposition rate.

Figure 3 shows the AES depth profiles of the HfN films deposited at -100 V_b. The AES results confirm that nitrogen was successfully incorporated into the film. The films show a relative composition of Hf:N = 0.55:0.45 at the surface.

Figure 4 shows the XRD pattern observed from the HfN film deposited under varying conditions with respect to V_b. It is

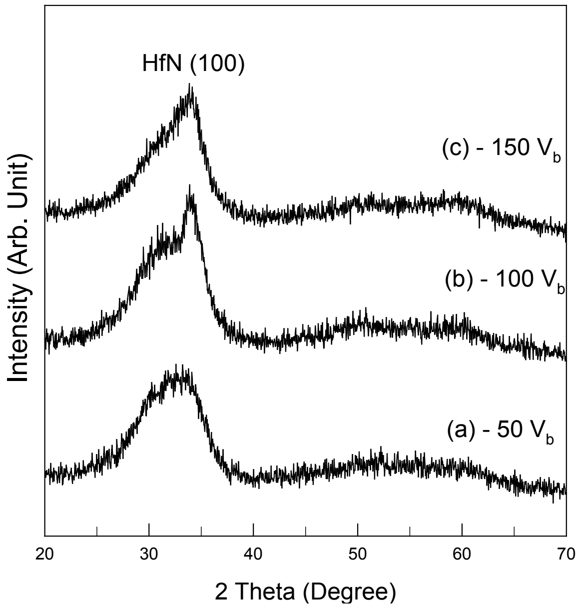

Fig. 4. X-ray diffraction pattern observed from the hafnium nitride (HfN) film deposited under varying conditions with respect to V_b.

known that the grain size (D) can be evaluated using the below equation [7],

$$D = 0.9\,\lambda/B\,\text{Cos}\Theta$$

where, λ is the wavelength of the incident X-ray, B is the full width half maximum (FWHM), and Θ is the diffraction angle; it is assumed that the grain size (D) increases as FWHM (B) decreases. In Fig. 4, films deposited under conditions of 100 V_b (bias voltage) exhibited narrower diffraction peaks in the HfN (100) plane than other films. It is well known that the FWHM values (for 2Θ) in the XRD pattern reveal the crystallinity of the film [8]. Although the grain size was not evaluated in this study, it is supposed that films deposited at -100 V_b have larger grains than those deposited at 150 V_b. In a previous study it was reported that intense ion bombardments cause a reduction in the grain size due to the enormous nucleation seed density [9]. Thus, intense bombardments may also produce complex defects that hinder crystallization.

Figure 5 shows AFM images of HfN films deposited under varying conditions with respect to V_b (bias voltage). In general, the surface roughness is decreased for the refined grain structures, while the RMS surface roughness is increased with respect to $-V_b$ in this study. The highest roughness of 6.7 nm is observed at a bias voltage of -150 V_b. The increment of surface roughness is attributed to re-sputtering with ionic bombardments that are too intense

4. CONCLUSIONS

An ICP-assisted magnetron sputtering system was used to deposit HfN films. In order to investigate the effect of substrate bias voltage, the films were deposited under varying conditions with respect to substrate bias voltage without intentional substrate heating.

As the bias voltage is increased, the crystallization in the HfN (100) plane is increased. However the crystallization decreased above 150 V_b due to intense N^+ ion bombardments. The AFM images also show that the surface morphology and roughness of the films were affected by the substrate bias voltage.

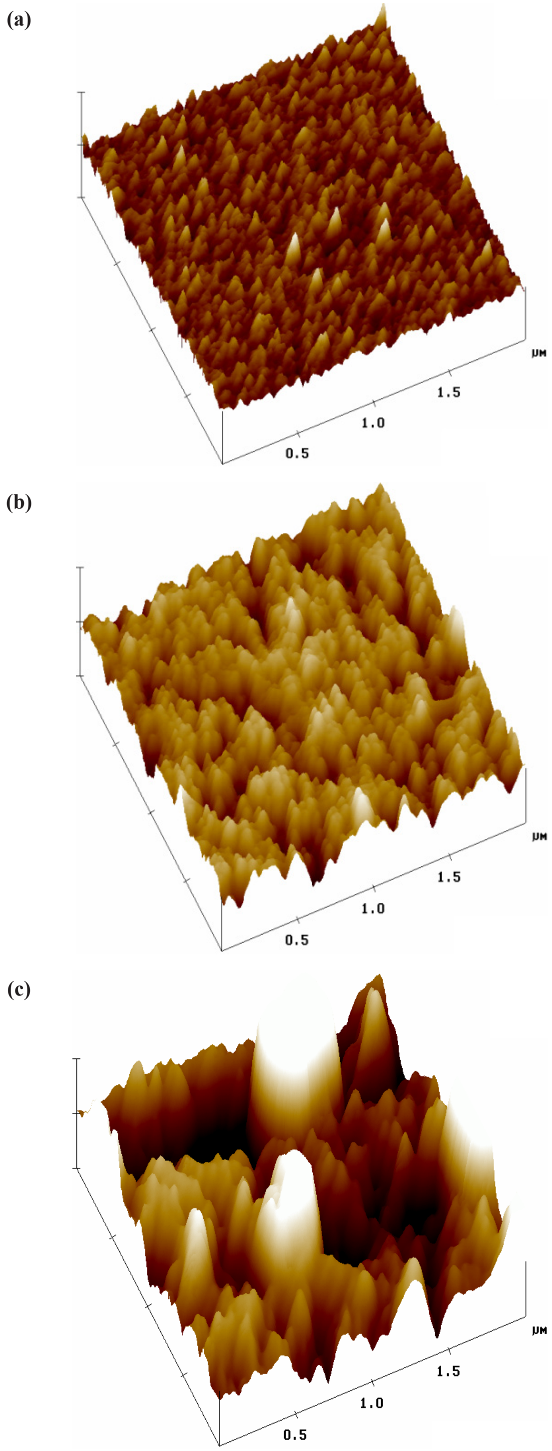

Fig. 5. Atomic force microscope images observed from the hafnium nitride film deposited under varying conditions with respect to V_b. (a) 50 eV (RMS; 0.8 nm), (b) 100 eV (RMS; 1.6 nm), (c) 150 eV (RMS; 6.7 nm). RMS: root mean square.

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