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Crystalline structures and electrical properties of high nitrogen-content Hf-Si-N films

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1. Introduction

Transition metal (TM) - silicon (Si) - nitrogen (N) alloys often have amorphous states, so they have been investigated as boundary-less barrier metals in multilayer Cu interconnects and metal gate materials with very small workfunction variations in recent years [1-5]. Although nanocrystallites often segregate in those films after post-deposition annealing (PDA) treatments at high temperatures, such a mixed structure of amorphous layer and nanocrystallites can be regarded as a uniform material if nanocrystallites are sufficiently dense and small compared to sizes of gates or interconnects. Control of size, density and crystalline structures of nanocrystallites are essential to control the electrical properties of the amorphous TM-Si-N films.

In previous papers, we have reported crystalline structures and electrical properties of the Ti-Si-N and Hf-Si-N MOS metal gates [5-7]. At low N contents, their resistivity increases with increasing the N content due to increase of Si_3N_4 component and development of amorphization. In contrast, at high N contents, N-content dependence of their resistivity is very different. With increasing N_2 concentrations of the sputtering ambient, the Ti-Si-N resistivity decreases although their N contents hardly change. Results of X-ray photoelectron spectroscopy (XPS) indicate that it is due to formation of Ti_3N_4. On the other hand, the Hf-Si-N resistivity is too high to be measured by the four-probe method. However, crystalline structures and electrical properties of such the high-N-content Hf-Si-N are not clear yet. In this study, current conduction properties characteristics of Pt/Hf-Si-N/Pt capacitors and crystalline structures of the high-N-content Hf-Si-N films were investigated in detail.

2. Experimental Procedure

Metal-insulator-metal (MIM) capacitor structures having Hf-Si-N films with various N contents were fabricated by magnetron sputtering. Platinum (Pt) was used as top and bottom electrodes. Hf-Si-N films were deposited on Pt/Ta/SiO_2/Si substrates by co-sputtering using Hf and Si targets in an N_2/Ar mixture ambient at room temperature. The N_2 concentration [N_2/(Ar+N_2)] of the sputtering ambient was varied from 0.0 to 43%. The thicknesses of the deposited films were 98 to 325 nm. After the deposition of the top Pt electrodes, some samples were subjected to PDA in a N_2 ambient at temperatures ranging from 500 to 900°C for 30 s.

3. Results and Discussion

Fig. 1 shows the resistivity values of the as-deposited Hf-Si-N films as a function of the N_2 concentration of the sputtering ambient. Plotted values below and above 10% of N_2/(Ar+N_2) were obtained by four-probe-method for Hf-Si-N/SiO_2/Si samples and I-V measurements for Pt/Hf-Si-N/Pt capacitors, respectively. As is clearly seen in the figure, as N_2 concentration increases above 10%, the resistivity drastically increases more than 10^5 times. Fig. 2 shows X-ray diffraction (XRD) profiles of the Hf-Si-N films deposited on the SiO_2/Si substrates [6]. In the case of the N_2 concentrations of 0% and 4.8%, diffraction peaks indicate crystalline phases of well-known Hf-nitrides (HfN, Hf_3N_2, Hf_4N_3) and Hf-silicides (Hf_5Si_3, Hf_5Si_4). On the other hand, at the N_2 concentrations of 9.0% and 43%, they are detected at lower angles (approximately 32° to 33°). They do not correspond well to the reported values of the foregoing nitrides and silicides. Except for those Hf-nitrides, Hf_3N_4 is also prospective to exist by numerical simulation [6]. Then, these diffraction peaks seem to agree best with Hf_3N_4 rather than the other phases of Hf-nitrides [6].

Fig. 3 shows cross-sectional TEM images and a TED pattern of the Hf-Si-N sputtered in the 43% N_2 ambient after PDA at 500°C. A halo ring appearing in the TED pattern indicates an amorphous state in the film. However, uneven contrasting density is found in the TEM image, and about-2-nm-sized nanocrystallites are observed in the darker regions. This result agrees with the crystalline grain size obtained using the Scherrer's formula from X-ray diffraction peaks. Therefore, nanocrystallites and amorphous layers were mixed in the Hf-Si-N film.

Fig. 4 shows valence and Hf4f photoelectron spectra of the Hf-Si-N deposited in 4.8, 9.0, and 43% N_2 ambient, whose thicknesses are 6.0, 6.0 and 10.0 nm, respectively. The binding energies were calibrated using the SiO_2 peaks in the O1s spectra at 533 eV. In the cases of the N_2 concentrations of 9.0% and 43%, the intensities of the valence photoelectrons are found to rise up at about 2.5 eV higher binding energies compared to the case of the 4.8% N_2 concentration. At the same time, main peaks of Hf4f also shift toward the higher energy binding side with increasing N_2 concentration. This suggests change of dominant binding states of Hf atoms from Hf-Si to Hf-N. Therefore, these results indicate that the Hf-Si-N formed in more than 9.0% N_2 ambient consisting of Hf-nitrides rather than Hf-slicides. They might have energy bandgaps, as is suggested for Hf_3N_4 by numerical computation [9].
Fig. 5 shows current density-electrical field and current density-voltage(J-V) characteristics of Pt/Hf-Si-N/Pt capacitors, in which the Hf-Si-N films were deposited at 13 %((a), (b)) and 43%((c), (d)) N_2 ambient, respectively. After PDA at 700°C, almost linear J-V characteristics are found regardless of N_2 concentration (Fig. 5(b) and 5(d)). In the case of the sputtering in 13% N_2 ambient and PDA at 500°C, a current conduction characteristic appears as a straight line in a Schottky plot ($\ln(J)$-$E^{1/2}$). In the case of the sputtering in 43% N_2 ambient and PDA

at 500°C, hysteresis loops are repeatedly observed in the J-V characteristics. In addition, amount of current densities and hysteresis characteristics are independent to electrode sizes. Therefore, these hysteresis characteristics are similar to a bipolar-type resistive switching behavior, which is well known as resistive random access memory (ReRAM) [9]. In general, such the resistive switching is observed for binary TM-oxides and perovskite ternary oxides. These suggest that the high-N-content Hf-Si-N consisting of Hf_3N_4 has semiconductive feature and Schottky junction is formed at Pt/Hf-Si-N interface.

4. Conclusions

Crystalline structures and electrical properties of the Hf-Si-N with high N contents have been investigated in detail. XRD profiles suggest the Hf_3N_4 phase in those films. According to XRD profiles and TEM images, there are about-2-nm-sized nanocrystallites in the Hf-Si-N films sputtered in the 43% N_2 ambient. Furthermore, valence photoelectron spectra indicate that there are energy bandgaps in such the high-N-content Hf-Si-N films. The current density-voltage characteristics of the Pt/Hf-Si-N/Pt capacitors, in which the Hf-Si-N films were sputtered in the 13% and 43% N_2 ambient and annealed at 500°C, show conductive characteristics of Shottoky emission and hysteresis loops, respectively. This hysteresis characteristic seems similar to the bipolar-type resistive switching behavior at a metal/semiconductor interface. Therefore, these results suggest that Hf_3N_4 and Hf-Si-N including Hf_3N_4 have semiconductive properties.

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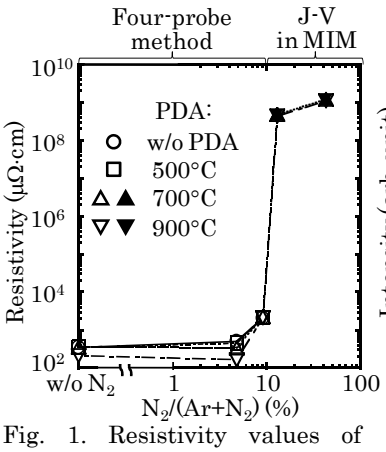

Fig. 1. Resistivity values of as-deposited Hf-Si-N films as a function of the N_2 concentration of the sputtering ambient.

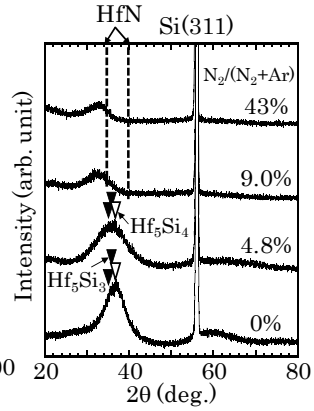

Fig. 2. XRD profiles of the Hf-Si-N films deposited on the SiO_2/Si substrates.

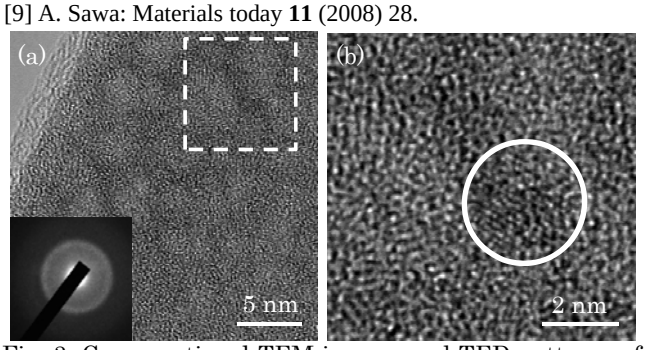

Fig. 3. Cross-sectional TEM images and TED patterns of the Hf-Si-N sputtered in the 43.0% N_2 concentration at 500°C.

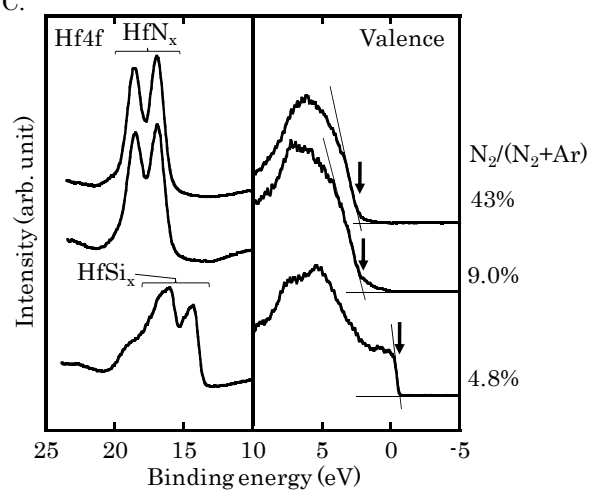

Fig. 4. Valence and Hf4f photoelectron spectra of the Hf-Si-N deposited in 4.8, 9.0, and 43% N_2 ambient.

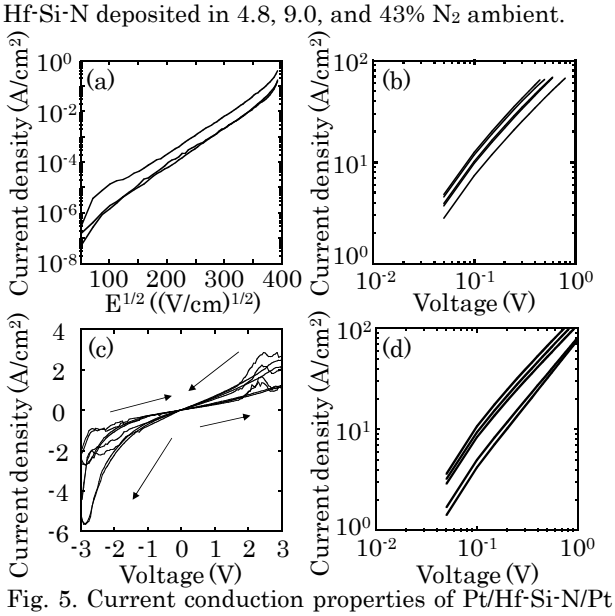

Fig. 5. Current conduction properties of Pt/Hf-Si-N/Pt capacitors, in which Hf-Si-N films were deposited at 13%((a), (b)) and 43%((c), (d)) N_2 ambient, respectively. PDA treatments were performed at 500°C ((a),(c)) and 700°C ((b),(d)), respectively.