Improvement of ultrathin Hafnium oxynitrides deposited on Si-substrate by adding gas ratio of N_2/O_2

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Abstract

An investigation of the electrical and physical properties of the HfO_xN_y films in the mixtures of different gas are presented for applications in MOS devices. The HfO_xN_y films were deposited onto n-type Si substrates by sputtering using mixture of N_2+O_2 and N_2O+O_2, respectively. Electrical measurements included current-voltage and capacitance-voltage measurements, and physical measurements included X-ray photoelectron spectroscopy (XPS). Films made by deposited in N_2+O_2 ambient showed better leakage current behavior, demonstrating that more nitrogen content can suppress the leakage current.

Key words: Hafnium oxide; HfO_xN_y; C-V; I-V; XPS

1. Introduction

Because of high direct tunneling current, the use of SiO_2 thinner than 2.0 nm may be quite challenging in future CMOS (complementary metal oxide semiconductor) devices [1]. As an alternative to oxide/nitride systems, much work has been done on high-K metal oxides as a means to provide a substantially thicker (physical thickness) dielectric for reduced leakage current and improved gate capacitance [2]. However most of the high-K materials e.g. TiO_2 and Ta_2O_5, are not thermally stable in direct contact with Si and then silicon oxide layers are formed at interfaces [3]. Among these dielectrics, HfO_xN_y appears to be promising due to its high-K value, thermally stable when contact with silicon substrate. HfO_xN_y shows significant reduction in leakage current density, boron penetration, superior thermal and electrical stability [4]. In this work, high quality of hafnium oxynitride (HfO_xN_y) gate dielectric prepared by annealing at temperature 450℃ and sputtering in different gas mixture of N_2O ＋O_2 and N_2＋O_2 are compared.

2. Experimental

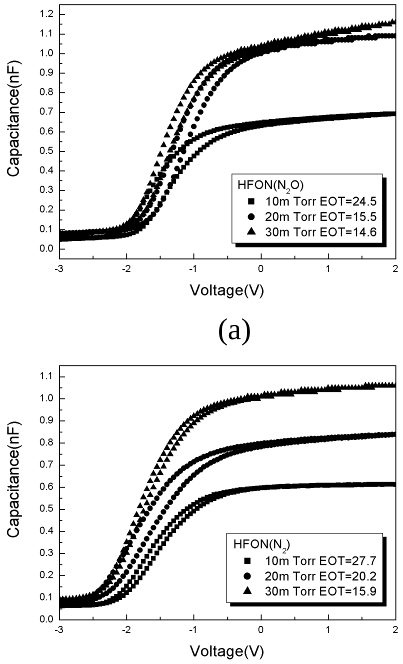
MIS capacitor structures with HfO_xN_y dielectrics were fabricated on silicon substrates. The n type (100) silicon wafers were cleaned with phosphorous acid , ethanol and deionized wafer, and then etched with HF solution (CH_3CH_2OH:HF ＝ 4:1). HfO_xN_y thin films were deposited through two steps [5]. First, Hf metal was pre-deposited in $N_2O＋O_2$ ambient and then a thin HfO_xN_y layer was deposited in $N_2＋O_2$ ambient from Hf metal target at room temperature with a power of 100 W. These samples were then annealed in N_2 ambient using a annealing furnace at temperature 450℃ for 30 minutes. Al sputtering was carried out at room temperature and a power of 100 W for 30 minutes. The samples were sputtered at three different kinds of deposition pressure, 10 mtorr, 20 mtorr, and 30 mtorr.

3. Result and Discussion

We examined the characteristics of HfO_xN_y films deposited by two different kinds of gas mixture in three different kinds of deposition pressure, as shown in Fig. 1(a) and (b).

The equivalent oxide thickness (EOT) of HfO_xN_y films was about 14.5Å (30 mtorr) to 25 Å (10 mtorr) in N_2O+O_2 ambient and 15.9Å (30 mtorr) to 27.7Å (10 mtorr) in N_2+O_2 ambient.

We can find that the EOT was reduced with increasing of deposition pressure. We also observed that the capacitance of HfO_xN_y films in N_2O+O_2 ambient were similar to those in N_2+O_2 ambient. In the Fig. 2(a) and (b) show the *I-V* curves of Al/HfO_xN_y/Si structure. There exists a significant difference in leakage current.

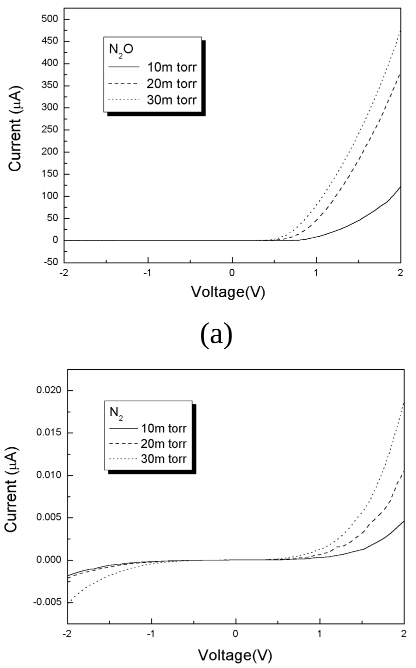


(a)

(b)

Fig. 1.The measurement of C-V curves at different mixtures of gas (a) N_2O+O_2 and (b) N_2+O_2.

The samples deposited in N_2+O_2 ambient show well-behaved leakage current characteristic. The leakage current in N_2+O_2 ambient at 1.5 V was about 5.86×10^{-9} A/cm^2, which was about there orders smaller than that in N_2O+O_2 ambient. Consequently, we were able to confirm that the leakage current of HfO_xN_y films deposited in N_2+O_2 ambient was improved.



(a)

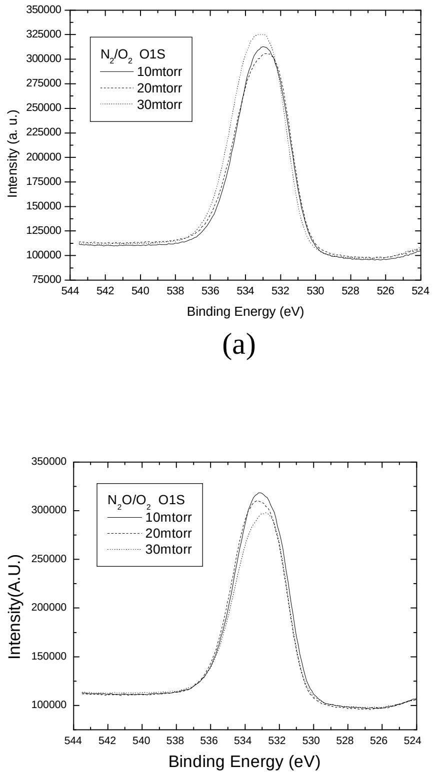
(b)

Fig. 2.The measurement of I-V curves at different mixtures of gas (a) N_2O+O_2 and (b) N_2+O_2.

Fig. 3. (a) and (b) show the O1*s* features by using the different gas ratios of N_2/O_2 and N_2O/O_2 , respectively. From fig.3.(a),we clearly observed the peak of silicate bonding at around 533 eV, which is associated with the bonding of Si-O-Si and Hf-O-Si rather than the metal oxide bonding. By increasing the deposition pressures, the intensity of peak position is also enhanced. On the contrary, as shown in fig. 3(b), by increasing the deposition pressures, the intensity of peak is reduced. A similar trend is also shown in fig. 4(a) and (b) for the Si 2*p* features, which exhibit a feature of double peak in the spectra. The position of the major peak is close to the Si-O bonding at 103.3 eV, but there is no adequate signal for the Si-N bonding to be was detected. In fact, a small signal was still detected in N1*s* spectra (which is not shown in this paper), in which nitrogen play important role in improving the electrical characteristics. It is suggested that the nitrogen signal need to be further studied on the annealed HfO_xN_y samples. As shown in fig. 4 (b), we observe that the intensity of the peak decrease with the increasing of the deposition pressures.

4. Conclusion

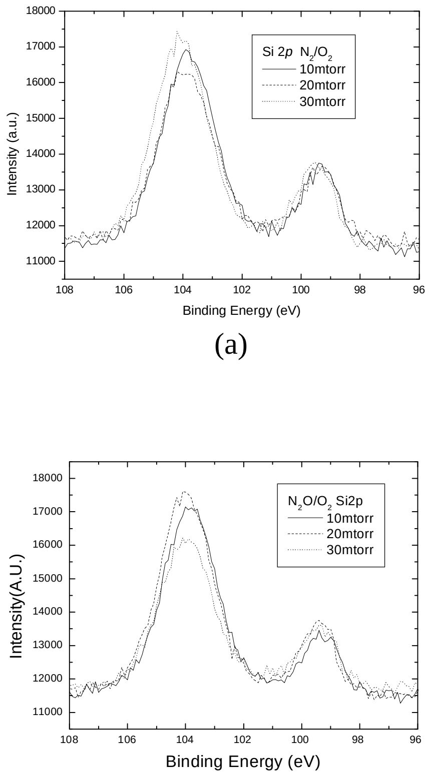
In this paper, we have compared the electrical characteristics of HfOxNy thin films at different gas ratios for mixtures of N_2O+O_2 and N_2+O_2. The leakage current of films in N_2+O_2 ambient was three order less than those in N_2O+O_2 ambient. However, the leakage current increases with the increasing of deposition pressures. Nonetheless, the XPS spectra of Si 2*p* peaks have no adequate signal to confirm the exited of Si-N bonding. Further investigation on the HfO_xN_y samples should be performed in order to confirm the incorporation of nitrogen in the HfO_xN_y films.



(a)

(b)

Fig. 3. XPS spectra of O1s for HfO_xN_y films with the (a) N_2 and O_2 (b)N_2O and O_2 forming gases was performed at room temperature



(a)

(b)

Fig. 4. XPS spectra of Si2*p* for HfO_xN_y films with the (a) N_2 and O_2 (b) N_2O and O_2 forming gases was performed at room temperature

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