The effect of atomic oxygen treatment on the oxygen deficiencies of Hafnium oxide films

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We have demonstrated the improvement of Hafnium oxide (HfO_2) films via atomic oxygen post-treatments. The films were characterized using spectroscopic ellipsometry (SE), synchrotron X-ray reflectivity (XRR), and Doppler broadening spectroscopy (DBS) of positron annihilation radiation. The results indicated that the O deficiencies in HfO_2 films greatly decreased after the treatment. It approved that atomic oxygen post-treatment is an effective method to improve the properties of HfO_2 films. Moreover, the proper treatment conditions should be necessary. This research provides a new insight for the preparation of high quality oxide films.

1. Introduction

Hafnium oxide (HfO_2) has been extensively studied as the dielectric layer in MOS devices [1-3] and optic coatings in many extreme environments [4-6], because of its excellent properties such as wide band gap, high dielectric constant, and good thermal and chemical stabilities. Generally, these properties can be affected by many factors [7, 8], among which the O deficiency is one key factor that often greatly impacts on the dielectric constant and transmittance of the films [9-11]. So far, many approaches have been employed to modify the O deficiencies in HfO_2 films, such as post- annealing [12, 13], surface passivation by one certain element [14-16]. However, these methods will often bring about the increase of the grain size within the films or introducing some other impurities into the samples.

Recently, atomic oxygen has attracted much attention during the growth of the HfO_2 film materials due to its strong oxidization ability [17, 18]. Grown by atomic oxygen deposition, the stoichiometric HfO_2 films are obtained and posses perfect dielectric properties. Moreover, atomic oxygen is known to universally abound in the Near-Earth space. So the investigation on the atomic oxygen treatment of the films is also very meaningful to the device stabilities in the spacecrafts [19, 20].

In this work, we aimed to use atomic oxygen to modify the O deficiencies within HfO_2 films deposited by pulsed DC sputtering. To our best knowledge, it is not previously reported to treat the sputtered HfO_2 films via atomic oxygen treatment. Spectroscopic ellipsometry (SE), X-ray reflectivity (XRR), and Doppler broadening spectroscopy (PADBS) of positron annihilation radiation were employed to investigate the O deficiencies within the HfO_2 films. The results showed that atomic oxygen treatment was effective to reduce the O deficiencies in HfO_2 films.

2. Experimental

HfO_2 films were prepared by reactive sputtering with a pulsed DC power supply. The pulse frequency of the supply was fixed to 40 KHz, the sputtering power was set to 42 W, and the duty factor was set as 70%. An Hf metal plate (purity > 99.995%) with diameter of 90 mm was used as the target. Prior to deposition, the chamber was pumped down to the pressure of 2.0×10^{-3} Pa by a turbo molecular pump. Then a gas mixture of O_2 (purity > 99.99%) and Ar (purity > 99.99%) was introduced to the sputtering system, and the flow rates of O_2 and Ar were 10 sccm and 28.3 sccm, respectively. The pressure of the system was kept to 1.0 Pa. The deposited time was set as 1 hour.

After deposition, the samples were treated by atomic oxygen in a home-made system as schematically illustrated in Fig. 1. The O_2 gas has been introduced into the quartz tube to produce the oxygen plasma when an rf power of 180 W was supplied to the helix copper coil. The plasma usually consisted of O^+ ion, O atom, O_2, etc. The O^+ ion was neutralized by the negative DC voltage supplied on the Mo plate in order to obtain more O atoms. The samples were treated at the different negative voltage of -20 or -30 V. The treatment time was 4 hours in our experiments.
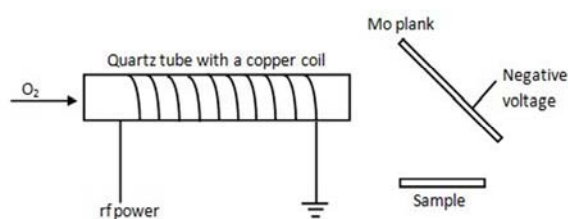
Fig. 1. The schematic diagram of the system used for the atomic oxygen treatment.

To study the optical properties of HfO_2 films treated by atomic oxygen, SE was measured in the range of 430 - 850 nm with an incident angle of 70° using MM-16 Liquid Crystal Modulation Ellipsometer (Horiba Jobin Yvon; Paris, France). The refractive indexes of the films were determined from SE data using Tauc-Lorentz model [21, 22]. XRR was measured on Beijing synchrotron radiation facility (BSRF; Beijing, China). The incident angle varied from 0 to 0.6^o with a θ-2θ scaning model using x-ray with the wavelength of 0.154 nm. The angular resolution of the measurement is 0.0025^o with respect to the samples planes. DBS measurements were taken using a ^{22}Na slow positron beam line with a high-purity Ge detector. Slow positrons with energy of 0.18~25.18 keV were implanted into the samples. Each spectrum was collected with a total count of about 5×10^5. S parameter was defined as the ratio of the counts in a central region of the annihilation peak (510.56–511.44 keV) to the total counts in the annihilation peak, and W parameter was obtained via dividing the summed counts in the high momentum region (505.05–508.5 and 513.5–516.95 keV) by the total count in the annihilation peak.

3. Results and discussion

Fig. 2 shows the refractive indexes of the as-deposited and the post-treated HfO_2 films as functions of the photonic energy. It can be seen that the refractive indexes of the samples slightly decrease after the atomic oxygen treatment. Generally, two aspects can account for this phenomenon. One is that the low refractive index usually implies the low density [23]. So the densification of the samples maybe decreases after the atomic oxygen treatment, which can be attributed to the bombardment of the particles against the film surface [24]. While the low voltage applied to neutralize the charged O ions cannot provide enough energy for the particles to bombard the samples. Thus, this reason can be negligible. The other is the enhanced oxidization of Hf atoms in the samples after the atomic oxygen treatment. In view of Zheng *et al*'s result [25], the refractive indexes of the samples often decrease with the band gap increasing, and the increasing band gap can be caused by the increase of oxidization. So, the samples after atomic oxygen treatment are more oxidized than the as-deposited ones. Accordingly, it can be concluded that atomic oxygen treatment can further

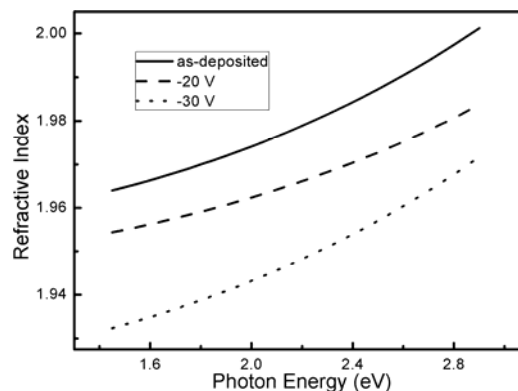oxidize the Hf atoms and reduce the O deficiencies in the samples.

Fig. 2. The refractive index of the as-deposited HfO_2 film and the post-treated films by atomic oxygen at the voltage of -20 V and -30 V, respectively.

To further verify the point above, both XRR and DBS were used to characterize the samples. Fig. 3 shows the XRR of the as-deposited and post-treated HfO_2 films as functions of the incident angles. The total reflective angle is marked by the dash line. It can be observed from Fig. 3 that the total reflective angle of the samples after treated by atomic oxygen becomes bigger than that of the as-deposited ones. According to the Parratt model [26], the total reflective angle is usually in direct proportion to the density of the samples. So, it can be deduced that the treated samples are denser than the as-deposited samples. Moreover, the total reflective angle of the sample treated at -20 V is larger than that of the samples at -30 V. This result indicates the samples treated at the voltage of -20 V possess a higher density, which implies a lower O deficient state density.
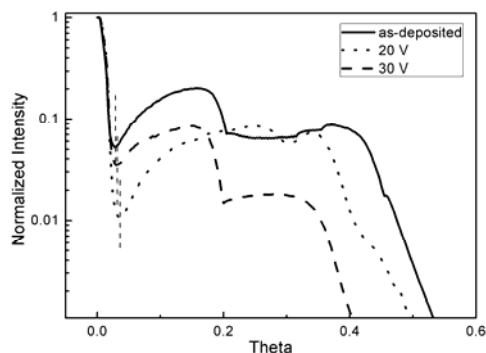

Fig. 3. XRR data of the as-deposited HfO_2 film and the post-treated films by atomic oxygen at the voltage of -20 V and -30 V, respectively.   The position of the total reflective angle is marked by the dash line.

Fig. 4(a) shows the values of S parameter (S values) of the as-deposited and post-treated HfO_2 films as functions of the incident positron energy. The analysis was

based on a four-layer structure of the HfO$_2$ films, which consist of the surface layer, HfO$_2$ layer, interfacial layer, and the substrate. Accordingly, the curves in Fig. 4(a) can be divided into four regions corresponding to the four layers of the samples. As for the first region from 0.18 keV to 1.18 keV, the S values are usually attributed to the annihilation of the positrons within the surface of the samples [27]. As for the second region from 1.18 keV to 8.18 keV, the S values are approximately constant, corresponding to the annihilation of the positrons in the HfO$_2$ layer of the samples. This region is mainly discussed in this paper. As for the third region from 8.18 keV to 22.18 keV, the S values increase monotonously as the positron energy increases. They could mainly be attributed to the annihilation of the positrons in the interfacial layer between the films and the substrates, which mainly consists of hafnium silicate, hafnium silicide, and silicon oxide [28-30]. The increase of S values indicates the decrease of Hf content and the increase of Si content in this region. When the incident positron energy is above 22.18 keV, the S values are a constant of 0.5. It is a typical value which is attributed to the annihilation of the positrons in the Si substrates. This indicated that the S values are mainly caused by the Si substrate used in our experiments when the incident positron energy is above 22.18 keV.
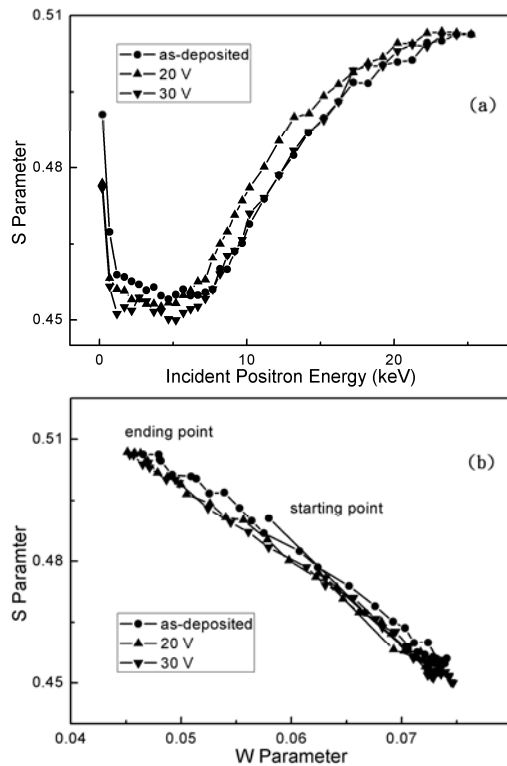

Fig. 4. (a) The S values (b) S-W curves of as-deposited HfO$_2$ film and the post-treated films by atomic oxygen at the voltage of -20 V and -30 V, respectively.

Compared the curves from the three types of samples, it can be found that the S values of the HfO$_2$ layer greatly decrease after the atomic oxygen treatment. S parameter mainly reflects the annihilation of positron with the low energy electron. Usually, when the positrons are trapped by the defects, such as the vacancies and open volume defects, a lager S value will be observed [31]. Thus, in our experiments, the change of S values can be attributed to the change of O deficiencies or open volume defects within the HfO$_2$ layer. The decrease of S values implies that the atomic oxygen treatment has greatly improved the O deficiencies or open volume defects within the HfO$_2$ layer. From our SE results, it can be seen that the refractive index decreased after the atomic oxygen treatment. According to the previous research, the refractive index will increase with the open volume defects decreasing. Thus, the decrease of S value cannot be assigned to the change of open volume defects, but to the decrease of the O deficiencies in the samples. This indicates that the atomic oxygen treatment is one effective method to reduce the O deficiencies in the samples.

Additionally, the S values of the sample treated at -20 V are smaller than that of the sample at -30 V. This result indicates that the sample treated at -20 V possess less O deficiencies. This well agrees with the above XRR analysis. Moreover, this result suggests that the choice of the neutralized voltage is also very important to our case. The excessively high neutralized voltage is unfavorable to improve the sample's quality because of the O atoms bombardment with induced bigger momentum by bigger voltage [24].

In addition, W parameter reflects the annihilation of positrons with high momentum electrons and is sensitive to the change in the electronic environment. So S-W relation can be used to characterize the type of the defects [32]. It can be seen from Fig. 4 (b) that all S-W curves for the three groups of samples showed a linear relationship, which indicate that the type of the defects in the samples was the same and did not change with different deposition conditions.

4. Conclusion

In summary, HfO$_2$ films have been prepared by the reactive sputtering supplied with a pulsed power and then treated by atomic oxygen at two different neutralized voltages. Analyses of SE, XRR, and PADBS results have indicated that the O deficiencies greatly decreased after the treatments. Our research suggests that atomic oxygen treatment is one effective method to decrease the O deficiencies in the films. Additionally, an appropriate neutralized voltage applied during the atomic oxygen treatments should be chosen. This research might provide a new insight for the preparation of high quality oxide films.

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