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Hafnium oxide thin films deposited by high pressure reactive sputtering in atmosphere formed with different Ar/O_2 ratios

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Abstract

The physical and electrical properties of hafnium oxide (HfO_2) thin films deposited by high pressure reactive sputtering (HPRS) have been studied as a function of the Ar/O_2 ratio in the sputtering gas mixture. Transmission electron microscopy shows that the HfO_2 films are polycrystalline, except the films deposited in pure Ar, which are amorphous. According to heavy ion elastic recoil detection analysis, the films deposited without using O_2 are stoichiometric, which means that the composition of the HfO_2 target is conserved in the deposition films. The use of O_2 for reactive sputtering results in slightly oxygen-rich films. Metal-Oxide-Semiconductor (MOS) devices were fabricated to determine the deposited HfO_2 dielectric constant and the trap density at the HfO_2/Si interface (D_{it}) using the high–low frequency capacitance method. Poor capacitance–voltage (CV) characteristics and high values of D_{it} are observed in the polycrystalline HfO_2 films. However, a great improvement of the electrical properties was observed in the amorphous HfO_2 films, showing dielectric constant values close to 17 and a minimum D_{it} of $2 \times 10^{11}\,eV^{-1}\,cm^{-2}$.

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Keywords: Hafnium oxide; Interface trap density; Sputtering

1. Introduction

The size reduction of complentary metal–oxide–semiconductor transistors (CMOS) has led to the study of alternative oxides with higher dielectric constants. Hafnium oxide (HfO_2) is a good alternative due to its suitable conduction band offset [1] and its thermal stability in contact with silicon [2]. HfO_2 may replace SiO_2 as gate dielectric only if the SiO_2 interface layer thickness, usually formed during HfO_2 deposition, is controlled and kept below 1 nm.

In this paper, we have chosen the novel high pressure reactive sputtering technique (HPRS) [3] to deposit HfO_2 films. This non-conventional deposition method works at pressures close to 1 mbar, three orders of magnitude higher than that for the conventional technique. The mean free path length of the plasma species is much shorter than the target to substrate distance, so that sputtered energetic

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atoms are thermalized before reaching the substrate and the growing film, avoiding damage of the interface.

2. Experimental

The physical properties of HfO_2 deposited by HPRS from a HfO_2 target with a nominal purity of 99.995% in atmospheres formed with different Ar/$(Ar+O_2)$ ratios (in the following, R) were studied. The depositions were performed during 30 min at a temperature of 200 °C on RCA-cleaned H-terminated n-Si substrates with a resistivity of 5 Ω cm.

All samples were characterized by transmission electron microscopy (TEM), electron dispersive X-ray spectroscopy (EDS), glancing X-ray diffraction (XRD), heavy-ion elastic recoil detection analysis (HI-ERDA) and Fourier transformed infrared spectroscopy (FTIR). MOS capacitors were fabricated with an e-beam evaporated Al gate electrode (capacitor area 10^{-3} cm^2) and characterized by means of the high–low frequency capacitance method [4]. This accurate and fast method allows determining the energy distribution of the interface trap density (D_{it}), provided the leakage current is negligible compared to the displacement current. To meet this requirement, thick films (10–20 nm) were grown.

3. Results and discussion

Fig. 1 shows the TEM images of two representative samples, one deposited with $R = 0.15$ and the other one with $R = 1$ (deposited with Ar only). In the micrographs a dual-layered structure can be observed. EDS measurements showed that the top dark layer contained Hf and O, therefore it was identified as hafnium oxide (HfO_x). According to the images and the electron diffraction patterns, all HfO_x films deposited with O_2 or Ar/O_2 mixtures were polycrystalline, whereas the films deposited with pure Ar were amorphous. This result was confirmed by glancing XRD. In fact, Fig. 2 shows the XRD patterns of several samples. As can be seen in Fig. 2, where $R<1$, the XRD diagrams exhibit the characteristic peaks of the HfO_2 monoclinic phase, whereas for $R = 1$ the XRD pattern shows the amorphous character of this film.

The bright interfacial layers between the HfO_x film and the Si substrate were identified as SiO_2 by FTIR and EDS. Fig. 3 shows the FTIR spectra of several samples deposited in different argon/oxygen atmosphere. The absorption band observed between 1200 and 1000 cm^{-1} is characteristic of an asymmetric stretching vibration of the SiO_4 unit. The maximum is situated at 1064 cm^{-1} irrespective of R, except for the sample deposited with only argon. In this case, the maximum shifts to 1072 cm^{-1}. The shift to lower wave numbers with respect to the maximum of thermally grown SiO_2 (1074.5 cm^{-1}) is normally related to strain in the SiO_2 film [5]. The polycrystalline structure of the HfO_2 films deposited with oxygen-containing atmosphere may be responsible of the higher strain in the SiO_2 interfacial layer [6]. This can explain the shift to lower wave numbers. In the amorphous films, this strain is relaxed and the wavenumber for this films shifts to a value close to the thermally grown SiO_2. In the last part of the article we will see how this strain influences the interface trap density.

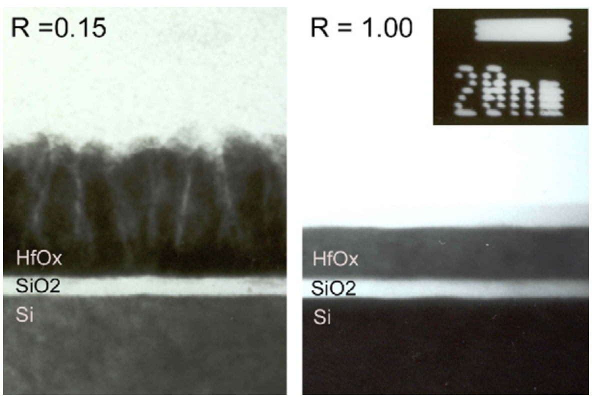

Fig. 1. Cross-sectional TEM images of the HfO_2 films deposited with different R values of 0.15 and 1.00. The scale of both images is the same.

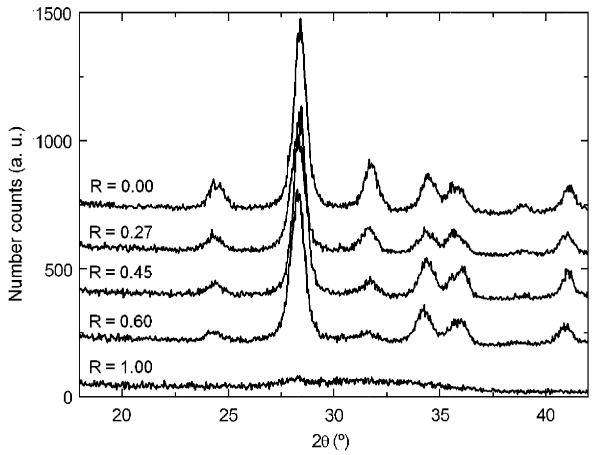

Fig. 2. XRD diagrams of HfO_2 films deposited with different R ratios.

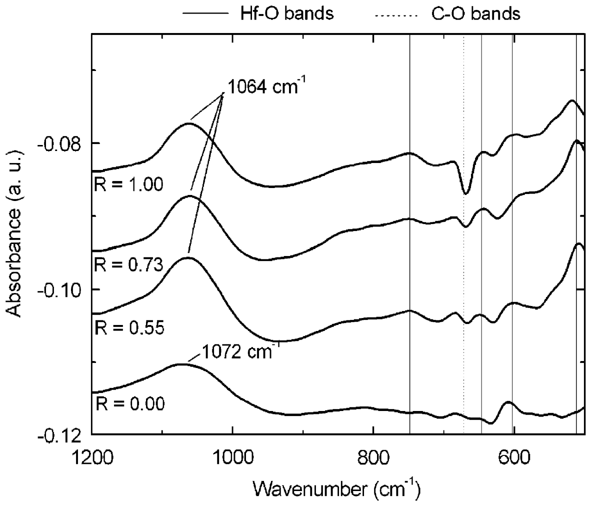

Fig. 3. FTIR spectra of the films deposited with different R ratios. The wave numbers of the main HfO_2 vibrations are highlighted with solid lines, and CO position with dashed lines. Si–O stretching band location for the different films is also indicated.

Fig. 3 also shows peaks situated at 748, 647, 601 and 512 cm^{-1} for the samples deposited with $R<1$, and a single peak at 601 cm^{-1} for the sample deposited with $R=1$. This result indicates that the peak situated at 601 cm^{-1} is related to amorphous and crystalline HfO_2, whereas the rest of the peaks are due to the HfO_2 monoclinic phase. This result shows that FTIR measurements can be used to check the crystalline structure of HfO_2 films.

The quantitative composition of the films was measured by HI-ERDA. In addition to Hf and O, significant amounts of H were found. The H concentrations were around 5% for the samples deposited with $R<1$, and 8% for the sample deposited with argon only. It was found that a big fraction of the H-content in the sample deposited with $R=1$ is situated at the interface according to the HI-ERDA measurements. Other impurities, such as B, C, N and F, were also detected with concentrations close to the detection limit of the HI-ERDA measurements (~0.1%). Excess of oxygen was observed with respect to the stoichiometric O/Hf ratio for the polycrystalline samples deposited with O_2 and Ar/O_2 mixtures with O/Hf ratio values around 2.2. On the other hand, near stoichiometric HfO_2 films were obtained in the samples deposited with Ar only (amorphous). The oxygen and hydrogen excess can be explained by the HfO_2 ability to adsorb moisture [7]. In the case of the HfO_2 polycrystalline films the moisture can be trapped by the dangling bonds of the grain boundaries, whereas in case of amorphous films the moisture can reach the substrate. This can explain the excess of oxygen in the polycrystalline samples, and the formation of the interfacial layer in the sample deposited with argon only. This will be discussed in the last part of the article.

In order to study the dielectric properties of the films, MOS capacitors were fabricated. Fig. 4 shows the quasistatic and 100 kHz CVs of the films shown in Fig. 1. The EOT value deduced from the accumulation capacitance was around 9 nm for the sample with $R=0.15$ and 6 nm for the sample deposited with $R=1$. The dielectric permittivities of the films were determined by modelling the capacitance of the sample as two series capacitances, one due to the SiO_2 interfacial layer and the other one due to the HfO_2 layer. Following this model, the permittivity of the HfO_2 can be calculated by means of

$$k_{HfO_2} = \frac{t_{HfO_2}}{(\varepsilon_0 A_{Al}/C_{Acc}) - t_{SiO_2}/\varepsilon_{SiO_2}}, \quad (1)$$

where t_{SiO_2} and t_{HfO_2} are the thickness of the SiO_2 and HfO_2 films, ε_0 and ε_{SiO_2} are the vacuum dielectric permittivity and the SiO_2 relative dielectric permittivity, A_{Al} the area of the Al electrode and C_{Acc} the capacitance measured in accumulation. The calculated k_{HfO2} value of this amorphous HfO_2 film was around 17, similar to values obtained with other deposition techniques [8]. Polycrystalline fims have k_{HfO_2} values in the 8–16 range.

Fig. 5 depicts the D_{it} extracted from the CV characteristics of Fig. 4. Similar poor CV curves

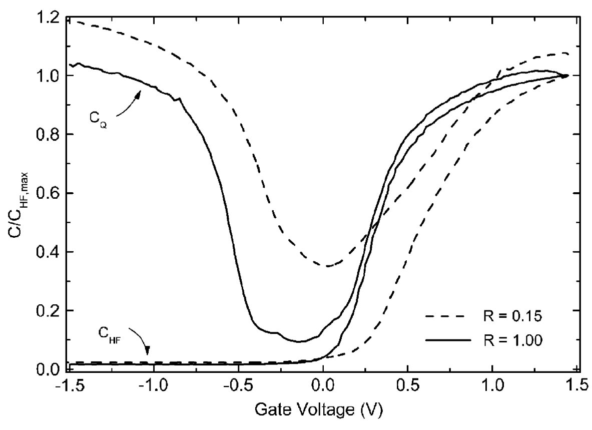

Fig. 4. Normalized high frequency (C_{HF}) and quasistatic (C_Q) CV characteristics for samples deposited with R = 0.15 (- - -) and R = 1 (—).

were observed in all samples deposited with oxygen. However, an important improvement was achieved in the samples deposited with argon only, diminishing the minimum D_{it} one order of magnitude to a value of $2\times10^{11}\,eV^{-1}\,cm^{-2}$, with the Fermi level sweeping a large part (0.88 eV) of the Si band gap. The peaks observed in the D_{it} distribution of Fig. 5, located at $E_c - E_t = 0.41\,eV$ and 0.73 eV can be related to the P_B-centre defects (a surface atom bonded to only three Si substrate atoms [9]). These are usually present at the SiO_2/Si interface. This indicates that the SiO_2 layer is the responsible of the interfacial properties of these samples.

The thickness of the SiO_2 interfacial layer that grows between the HfO_2 film and the Si-substrate is around 3.5 nm in all cases. The formation of the SiO_2 interfacial layer can be explained by two processes: an initial oxidation of the silicon substrate due to the effect of the oxygen plasma, and the moisture diffusion through the HfO_2 film. For the samples deposited with oxygen, the effect of the plasma oxidation is more important because there is a high concentration of O* radicals in the atmosphere. These radicals can reach the substrate, react with the silicon substrate and form SiO_2. On the other hand, the amorphous structure of the sample deposited with argon only allows the moisture diffusion through the HfO_2 films. The oxygen (of the hydroxyl groups –OH) arriving at the interface can promote the growth of the SiO_2 interfacial layer.

A possible explanation of the differences found in the D_{it} distribution of films deposited in Ar/O_2 atmosphere and those deposited with pure Ar can also be related to the moisture effect. The water diffusion process through the bulk HfO_2 film to the SiO_2 /Si interface may take place in different ways depending on the crystallinity of the HfO_2 films. We observed this by means of HI-ERDA. The diffusion is more effective in the amorphous films, and hydrogen that reaches the SiO_2/Si interface can play a passivation role and can be the responsible of the changes observed in Figs. 4 and 5. Besides, we observed by FTIR that the HfO_2 polycrystalline films induced strain in the SiO_2 interfacial layer. In the amorphous case, the SiO_2 stretching wave number is close to the un-strained value, which means that the strain is much smaller in this case. As a consequence, it could be concluded that the reduction of interface trap density is due to the release of the strain in the SiO_2 film and the passivation with hydrogen of the SiO_2/Si interface for the amorphous film. In any case, more work is now in progress in order to ellucidate the different behaviours observed in gate structures with HfO_2 polycrystalline films and those with amorphous ones.

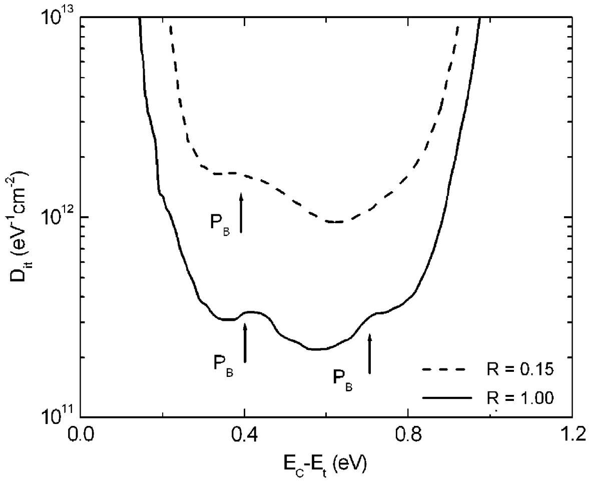

Fig. 5. Interface trap density (D_{it}) extracted from CV characteristics for samples deposited with R = 0.15 (---) and R = 1 (—). E_t is the energy level of the traps inside the gap and E_C stands for the energy of the conduction band.

As a consequence, the improvement of the electrical *C–V* characteristics (Figs. 4 and 5) can be explained by the structural differences mentioned above between the films deposited with O_2-containing atmospheres and the samples deposited with Ar only. As an additional comment, an amorphous gate dielectric is considered to be more suitable than a polycrystalline one, because polycrystalline materials present issues of structural anisotropy and great leakage currents through grain boundaries. With our HPRS system, the samples deposited with no oxygen are amorphous with smooth surface and an O/Hf = 2 ratio. However, because in a full CMOS technology the gate structure would experience high temperature activation processes (typically 1000 °C for 1 s), an amorphous HfO_2 film, like those described in this paper, is likely to recrystallize and, as a consequence, the benefits of the amorphous layer would be lost. Then, our approach could be useful only for a gate-last process.

4. Conclusions

The properties of HfO_2 films deposited by HPRS in different Ar/O_2 plasma mixtures have been studied. All samples deposited with O_2 or Ar/O_2 mixtures presented the same characteristics: polycrystalline morphology, oxygen excess and poor gate dielectric properties. However, the samples deposited with argon only were amorphous, stoichiometric and presented reasonably low interface trap density. Gate structures with our amorphous HfO_2 films may be used in CMOS technology if gate formation is the last process of CMOS technology and if SiO_2 interfacial thickness is reduced to 1 nm or below. Work to reach this objective is now in progress.

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