Improvement of interfacial and microstructure properties of high-$k$ ZrO$_2$ thin films fabricated by filtered cathodic arc deposition using nitrogen incorporation

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Abstract

We investigate the microstructure and interfacial characteristics of nitrogen plasma-nitrided ZrO$_2$ thin films deposited on $p$-type Si (100) wafers by cathodic arc deposition. The results show that the incorporation of a small amount of N into ZrO$_2$ can improve the thermal stability of the thin films. High resolution transmission electron microscopy micrographs further confirm that the nitrided film remains amorphous and the interfacial layer has been essentially suppressed. The effects and underlying mechanism are discussed.

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1. Introduction

Various kinds of high-$k$ materials have been explored to replace conventional silicon oxide or oxynitride in integrated circuits [1]. Due to its high permittivity and good thermodynamic stability in contact with silicon, zirconia (ZrO$_2$) is considered one of the most promising alternative materials and has been studied as storage capacitor material in dynamic random access memories (DRAMs) and as gate oxide in field effect transistors (FETs) [2,3]. However, undesirable crystallization of ZrO$_2$ at temperatures below 400 °C and degradation of the equivalent oxide thickness due to the formation of an interfacial layer limit the applications of the thin films in ultra large-scale integrated (ULSI) circuits [4]. This is because grain boundaries in crystallized gate dielectrics can be the fast paths for oxygen and dopant diffusion into the gate dielectric, causing a significant increase in both the leakage current and surface roughness [5]. It is well known that incorporation of nitrogen into ZrO$_2$ can promote the formation of covalent bonding in the thin films. Furthermore, accumulation of nitrogen atoms at the SiO$_2$/Si interface can improve hot carrier resistance, and the use of oxynitride is also known to suppress boron penetration from the poly-Si gate into Si [6,7]. Thus, nitridated oxides are attracting a great deal of attention in microelectronics, including not only flash memory devices but also standard metal oxide silicon (MOS) logic circuits. There have been several reports on incorporating nitrogen into binary metal oxides to improve the thermal stability by high temperature annealing in N$_2$O or NH$_3$ ambient [8,9]. Unfortunately, the high-$k$ dielectric materials nitrided by NH$_3$ exhibit an increased interfacial trapping density and a deterioration of mobility due to hydrogen-related traps (–H, –OH, and N–H) [10]. Besides, N$_2$O and NH$_3$ are both toxic gases. Therefore, the development of novel deposition technology that utilizes nitrogen instead of NH$_3$ and N$_2$O is preferred to achieve crystallization control of advanced gate dielectrics for a ‘clean’ ULSI process.

In this work, we investigate the microstructure and interfacial characteristics of plasma-nitrided ZrO$_2$ thin films deposited on $p$-
type Si (100) wafers by cathodic arc deposition. It is found that the incorporation of a small amount N into ZrO₂ increases the thermal stability of the thin films. High resolution transmission electron microscopy micrographs confirm that the nitrided layer remains amorphous and the interfacial characteristics are obviously improved. Our study suggests that plasma immersion nitridation in concert with cathodic arc deposition is an effective method to improve the microstructure of ZrO₂. This technique can be readily transferred to other high-k dielectric materials.

2. Experimental details

ZrO₂ thin films were fabricated on p-type, 100 mm thick Si (100) wafers with resistivity of 4–7 Ω cm using an N₂ plasma immersion nitriding and cathodic arc deposition system. The experimental apparatus used in this study mainly included a magnetic duct and cathodic arc plasma source and has been described elsewhere [11]. The cathode comprised a 99.9% pure Zr column with a diameter of 1 cm, and the working gas composed of a mixture of N₂ and O₂ was bled into the vacuum chamber at different flow rates at the vicinity of the exit of the metal arc discharge plume in order that the gas plasma should be simultaneously induced when the cathodic arc was triggered. The arc was ignited within the pulse duration of about 100 μs, with a repetition rate of 60 Hz. The amount of zirconium in the discharge was controlled by the main arc current between the cathode and anode [11]. For comparison, some ZrO₂ thin films were deposited using the same percent of argon instead of nitrogen. The chamber pressure was about 1×10⁻⁷ Torr and RF power of 100 W was applied for a time of 120 min.

Rutherford backscattering spectrometry (RBS) was carried out using a 2 MeV ⁴He⁺ beam and a backscattering angle of 170° to determine the composition as well as the thickness of the thin films. Microstructural analyses were done by a PERKIN ELMER Fourier transform infrared (FTIR) spectrometer and a Siemens D500/501 thin film diffractometer in a θ–2θ configuration and with a Cu Kα source. The cross-sectional microstructure of the thin films was examined by a Philips CM200 high resolution transmission electron microscope (HRTEM). Contact mode atomic force microscopy (AFM) was conducted on a Park Scientific Instrument (PSI) Autoprobe Research System to evaluate the surface morphology over a scanned area of 2 μm × 2 μm. Zr, O and N bonding information was acquired using X-ray photoelectron spectroscopy (XPS) employing monochromatic Al Kα radiation. Prior to the XPS analyses, the sample surface was cleaned by 4 keV Ar ion bombardment for 1 min to remove atmospheric contaminants.

3. Results and discussion

The elemental composition of the thin film influences the structure and electrical properties and RBS was used to characterize our materials. Table 1 displays the composition and thickness calculated from the RBS spectra. The results disclose the formation of stoichiometric ZrO₂ and that the composition of the thin films produced under different conditions is basically uniform throughout the thickness. These good results are in part due to the effective elimination of Zr macro-particles formed in the cathodic arc by the curved magnetic filter. The process efficacy can be evaluated according to the simulation results of the zirconium contents in the layer [11]. However, the elemental N concentration in the plasma-nitrided sample is very small as shown in Table 1. It is very close to the detection limit of RBS, that is, less than several atomic % [12]. Hence, the N content in our sample cannot be accurately determined by RBS. The XPS spectra show that the nitrogen concentration in the nitrided layer is about 0.5%. According to the report by Asahi et al. on nitrogen-doped

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Composition ratio (Zr:O:N)</th>
<th>Thickness (1×10¹⁵ atoms/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Zr:O=0.33:0.67</td>
<td>1400</td>
</tr>
<tr>
<td>(b)</td>
<td>Zr:O=0.33:0.67</td>
<td>1000</td>
</tr>
<tr>
<td>(c)</td>
<td>Zr:O:N=0.33:0.66:0.01</td>
<td>300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Transmittance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>Pure O₂</td>
</tr>
<tr>
<td>1800</td>
<td>O₂+Ar</td>
</tr>
<tr>
<td>2100</td>
<td>O₂+N₂</td>
</tr>
</tbody>
</table>

Fig. 1. FTIR spectra of ZrO₂ thin films prepared at 450 °C using different gases.

Fig. 2. XRD spectra of ZrO₂ thin films prepared at 450 °C using different gases.
titanium oxides, slight N doping can change the crystal structure and properties of the sample [13]. Besides, it can clearly be observed from the RBS results that the thicknesses of the thin films produced under different conditions are different. That is, the growth rate decreases as nitrogen is introduced.

Fig. 1 shows the Fourier transform infrared (FTIR) spectra of the ZrO$_2$ thin films on Si (100) deposited at 450 °C under different gas mixtures. The thin films produced with pure oxygen exhibit strong absorption peaks located near 580, 510 and 420 cm$^{-1}$ corresponding to the Zr–O vibrational modes [14,15]. Furthermore, the weak absorption bands at around 720 cm$^{-1}$ of Zr–O–Si and 800 and 1080 cm$^{-1}$ of the Si–O vibration mode imply the formation of little SiO$_x$ and ZrSiO$_x$ at the interface [16]. However, it is clearly seen that the Si–O absorption peaks almost disappear and the intensity of the Zr–O–Si absorption peaks diminishes significantly, indicating that

![Fig. 1. Fourier transform infrared (FTIR) spectra of ZrO$_2$ thin films on Si (100) deposited at 450 °C under different gas mixtures.](image)

with the addition of nitrogen radicals, the interfacial structure of the ZrO$_2$/Si thin films can be optimized. For comparison, the FTIR spectrum of the ZrO$_2$ thin films deposited using argon instead of nitrogen is also depicted in Fig. 1. No change can be found compared to the sample deposited with pure oxygen except that the intensity of the absorption peak is lower. This may be a consequence of the reduced growth rate due to the presence of argon. Our results suggest that by using employing

![Fig. 3. HRTEM images of ZrO$_2$ thin films prepared at 450 °C using (a) pure oxygen and (b) oxygen mixed with nitrogen.](image)

![Fig. 4. AFM images of ZrO$_2$ thin films prepared at 450 °C using different gases: (a) pure oxygen, (b) oxygen mixed with argon, and (c) oxygen mixed with nitrogen.](image)
plasma immersion nitridation, an interfacial layer with low permittivity can be suppressed, thereby boding well for the dielectric properties of the thin films.

The degree of crystallization of the thin films deposited at 450 °C using different gas mixtures is analyzed by X-ray diffraction (XRD) patterns and the results are shown in Fig. 2. It can be seen that the thin film produced with pure oxygen is crystallized, as indicated by the diffraction peaks at 29.95° and 34.83° in the spectrum corresponding respectively to the (111) and (002) planes of the orthorhombic ZrO₂ phase [17]. Similarly, for the thin films deposited using argon and oxygen, two diffraction peaks representative of the (111) and (002) planes emerge in the XRD spectrum. Nevertheless, the relative intensity of the diffraction peaks is lower, which may be due to the reduced deposition rate because of the addition of argon. In comparison, when nitrogen is introduced, the crystallized diffraction peaks are absent and there remain only one weak and broad band. It can be inferred that the thin film deposited with nitrogen is almost amorphous. Usually, ZrO₂ crystallizes at temperatures below 400 °C [4]. Our results suggest that N- incorporated ZrO₂ thin films exhibit enhanced thermal stability. The effect can be attributed to the breaking of the periodic crystal arrangement in the ZrO₂ lattice or the inhibition of continuous crystal growth in the nitrogen-doped materials.

In order to further verify the effects of plasma immersion nitriding on the microstructure of the ZrO₂/Si thin films, high resolution transmission electron microscopy (HRTEM) was conducted and the results are shown in Fig. 3. The TEM images confirm that the thin film deposited with pure oxygen exists as a polycrystalline phase whereas the nitrided sample remains almost amorphous, which agree with the XRD results. Furthermore, it can be clearly seen from the cross-sectional TEM images that the interfacial layers in the ZrO₂ thin film and nitrided sample are obviously different. That is, in the former, there is an interfacial layer with the thickness of 2 nm but no visible interlayer can be observed in the nitrided sample, which is consistent with the FTIR results. This can be attributed to the fact that N effectively blocks oxygen diffusion through the grain boundaries during the fabrication [18].

The surface morphology and roughness of the thin films were assessed by atomic force microscopy (AFM). Fig. 4 depicts the AFM images of representative samples prepared under different conditions. Crystallized particles on the thin films are clearly seen in Fig. 4(a) and (b). With the addition of nitrogen, an amorphous morphology emerges as shown in Fig. 4(c). As confirmed by the XRD results, the surface roughness of the nitrogen-doped thin film decreases substantially. It is well known that the surface roughness of gate dielectric thin films is an important factor influencing the electrical stability of MOS devices [19]. Based on the above results, it can be concluded that by using plasma immersion nitridation, the thermal stability and interfacial properties of ZrO₂/Si thin films can be improved. The simplicity of this method makes it easily transferable to the synthesis of other dielectric materials.

4. Conclusion

ZrO₂ thin films as an alternative gate dielectric in microelectronics were deposited by N₂ plasma immersion nitridation and cathodic are deposition. Incorporation of a small amount of N into ZrO₂ transforms the microstructure of the thin film, and the interfacial characteristics of the ZrO₂/Si thin films are obviously improved. Our study suggests that plasma immersion nitridation in conjunction with cathodic are deposition is an effective method to dope ZrO₂ with nitrogen and to improve the microstructure. The success may accelerate the acceptance of alternative high-k thin films in advanced integrated circuits.

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References