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Optical spectroscopic study of the SiN/HfO$_2$ interfacial formation during rf sputtering of HfO$_2$

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High-k stacks formed by chemical-vapor-deposited SiN and high-pressure sputtered HfO$_2$ in either O$_2$ or Ar atmosphere have been studied. The introduction of a SiN layer is proposed to prevent the uncontrollable SiO$_2$ growth while sputtering. The formation of Si–O bonds after the sputtering of the HfO$_2$ film in O$_2$ atmosphere was observed by infrared spectroscopy. Optical diagnosis of the plasma demonstrated a high density of O radicals in the system when working with O$_2$. The small radius and high reactivity of these O radicals are the source of the SiN oxidation. However, the structure of the SiN film is preserved during Ar sputtering. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2811958]

A great effort has been devoted in the past few years toward the growth of high-k dielectrics on silicon, trying to avoid the uncontrolled formation of a low-k interface layer. In particular, during sputtering of HfO$_2$, the appearance of a thick SiO$_2$ layer is always observed. Hence, introducing a proper barrier between the HfO$_2$ layer and the silicon substrate is critical to gain the benefits of the high-k dielectrics. SiN thin films have proven to be good diffusion barriers against oxygen and silicon.[1] Furthermore, they present moderate k values, suppress silicate formation, and act as metal and boron diffusion barriers.[2] In this work, the incorporation of a SiN buffer layer prior to the deposition of HfO$_2$ by high pressure sputtering (HPS) is researched. The bonding structure changes of this SiN layer were studied after the HfO$_2$ sputtering in both pure Ar and pure O$_2$ plasmas, which were previously found to produce amorphous or polycrystalline HfO$_2$ of monoclinic phase, respectively, as well as an interfacial silicon oxide layer.[3] Glow discharge optical spectroscopy (GDOS) is a powerful technique to analyze the composition of plasmas.[4] In this letter, this technique was used to understand the origin of the oxidation mechanism and the structural changes of the SiN buffer layer that occur during the HfO$_2$ sputtering.

The SiN buffer films were deposited on Si using a commercial electron cyclotron resonance reactor (Astex AX4500). N$_2$ and SiH$_4$ were used as precursor gases in a ratio of 9.1 with a total gas flow of 10.5 sccm. The deposition pressure was 9×10^{-4} mbar. The substrate temperature and the microwave power were 200 °C and 100 W. In these conditions, the growth rate and film thickness were 4.4 nm/min and 8.8 nm.

The HPS HfO$_2$ films were deposited on the SiN/Si structures to form HfO$_2$/SiN/Si stacks. This nonconventional sputtering procedure works at pressures about 1 mbar, reducing the mean free path of the plasma species, thus decreasing the substrate bombardment of the energetic species being reflected from the target.[5] A 99.95% nominal purity and 4.5 cm diameter HfO$_2$ target was used. The substrate

temperature and radiofrequency power were 200 °C and 60 W. The sputtering atmosphere was pure O$_2$ or Ar at a deposition pressure of 1.2 mbar. These conditions provided growth rates and film thicknesses of 0.5 nm/min and 14 nm.

The bonding structure changes of the SiN films after HfO$_2$ deposition were investigated by Fourier transformed infrared (FTIR) spectroscopy using a Nicolet Magna-IR 750 Series II spectrometer working in transmission mode at normal incidence, and by cross sectional transmission electron microscopy (TEM) with a JEOL-JEM-2000FX microscope operating at 200 keV. Both O$_2$ and Ar sputtering atmospheres were analyzed by GDOS. The emission lines of the rf-sputtering glow discharge were registered by a Jobin Yvon H-25 monochromator attached to a photon-counting system in the 250.0 to 650.0 nm range with a resolution of 0.01 nm.

Figure 1 shows the IR spectrum of the as-deposited SiN film (a), and the IR spectra of both HfO$_2$/SiN stacks deposited in Ar (b) and O$_2$ (c). No significant modifications related to SiN were found outside the 700–1200 cm^{-1} region. At lower wave numbers, the known HfO$_2$ bands were found.[3] The well-known asymmetric stretching vibration of the SiN absorption band between 750 and 970 cm^{-1} is observed in the SiN layer prior to the deposition of HfO$_2$. The maximum of the band is placed at 844 cm^{-1}, slightly above the fre-
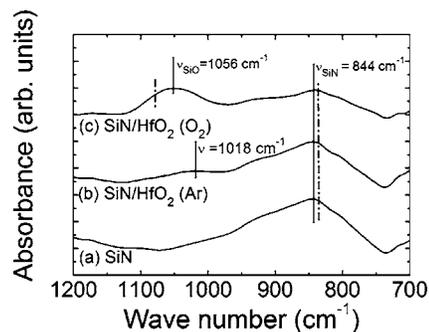

FIG. 1. FTIR spectra in the 1200–700 cm^{-1} region: (a) as-deposited SiN film, (b) SiN+HfO$_2$ deposited in Ar atmosphere, and (c) SiN+HfO$_2$ deposited in O$_2$ atmosphere. The wavenumbers are highlighted by dashed lines for stoichiometric SiO$_2$ and SiN, and by continuous lines for the values found in this paper.

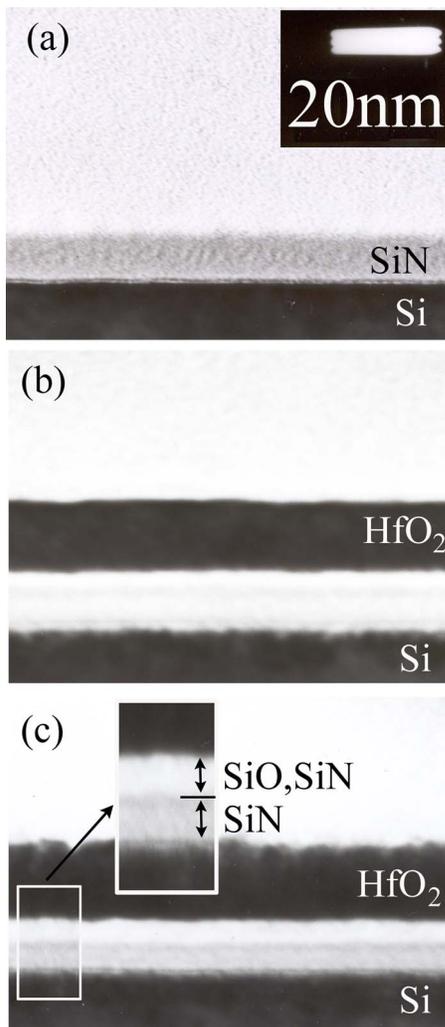a)Author to whom correspondence should be addressed. Electronic mail: mtluque@fis.ucm.es

FIG. 2. (Color online) Cross-sectional TEM images: (a) as-deposited SiN film, (b) SiN+HfO$_2$ deposited in Ar atmosphere, and (c) SiN+HfO$_2$ deposited in O$_2$ atmosphere.

FIG. 3. Optical spectra of HfO$_2$ sputtering: (a) pure Ar as sputtering gas and (b) pure O$_2$.

quency corresponding to the stoichiometric Si$_3$N$_4$ (835 cm^{-1}) and characteristic of N-rich SiN layers.[6]

In the HfO$_2$/SiN stack with HfO$_2$ deposited in Ar atmosphere [Fig. 1(b)], the HfO$_2$ sputtering does not alter the shape or intensity of the SiN band. A less intense band appears at about 1018 cm^{-1}, slightly above the wave number of the Si–O–Hf group (970 cm^{-1}) (Ref. 7) and below the wave number of the SiO stretching vibration (1075 cm^{-1}).[8] On the other hand, the intensity of the SiN stretching band at 844 cm^{-1} is reduced considerably in the spectrum of the HfO$_2$/SiN stack with HfO$_2$ deposited in pure O$_2$ [Fig. 1(c)]. Additionally, a new band appears at 1056 cm^{-1} (close to the ideal Si–O stretching vibration at 1075 cm^{-1}),[8] with an intensity comparable to the SiN band. The appearance of two clear separate bands, instead of a broad one, indicates the presence of two separate Si–N and Si–O phases, rather than the formation of SiON. The difference of the Si–O vibration with respect to the fully relaxed SiO$_2$ value is likely due to the stress produced by the polycrystalline character of the top HfO$_2$ film deposited in pure O$_2$.[3] Moreover, the decrease of the SiN band intensity suggests that during HfO$_2$ deposition in O$_2$, nitrogen in the SiN layer is being released and substituted by oxygen.

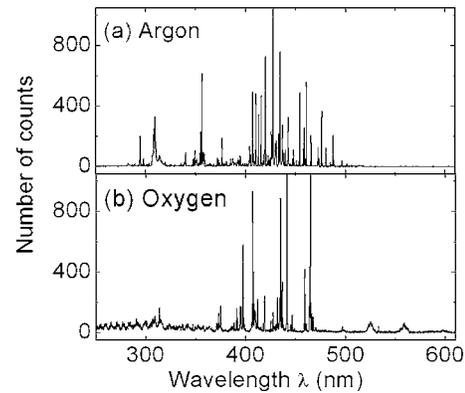To further study the Si–O bond formation during HfO$_2$ deposition in O$_2$ atmosphere, the HfO$_2$/SiN interface was analyzed by TEM. Figure 2(a) demonstrates the homogeneity of the as-deposited SiN film. Figure 2(b) shows that the SiN film is unaltered after the deposition of the amorphous HfO$_2$ film in Ar plasma. In contrast, Fig. 2(c) shows relevant changes when the polycrystalline HfO$_2$ layer is deposited in pure O$_2$: the homogeneity of the SiN layer is lost and an interfacial layer appears between the SiN and the HfO$_2$ [see inset of Fig. 2(c)].

TEM and FTIR results consistently demonstrate that the SiN structure is only affected by the HfO$_2$ sputtering in O$_2$, which leads to the formation of Si–O bonds. GDOS analysis was used to detect the chemical states of the species in the sputtering chamber in order to understand the observed SiN behavior during the HfO$_2$ growth in both Ar and O$_2$ atmospheres.

The optical emission spectrum during the Ar discharge is shown in Fig. 3(a). The main lines are due to Ar I, Ar II, Hf I, and Hf II. Table I lists the wavelengths of those emission lines, together with their associated E_k and E_l transition levels.[9,10] Additionally, an OH band was observed at 306.4 nm.[11] This strong emission band is frequently found in sputtering systems as well as in measurements involving hydrogen together with noble gases.[12] Significantly, neither distinct O line nor HfO band were observed in the spectrum. All the intense lines of the spectrum are due to either Ar or Ar$^+$, meaning that this HPS system is very efficient in the ionization and excitation of the Ar atoms. The de-excitation of the Ar atoms occurs via their metastable atomic states at 11.5 and 11.7 eV, and it is likely that the Ar ionization also takes place through these intermediate levels. Neutral and single ionized Hf atoms were also detected in the plasma, as shown in Table I, but no HfO groups were found. Therefore, Hf is sputtered as a single atom and diffuses to the substrate without oxidizing.

The GDOS results with pure O$_2$ atmosphere are shown in Fig. 3(b). The main lines are due to oxygen related species: O I, O II, and O$_2^+$. As opposed to the Ar case, no unambiguous Hf lines were observed in the O$_2$ spectrum. The wavelength of the main lines and their associated energy levels are listed in Table II. In our HPS system, the collisions involving electrons are dominant in determining the glow discharge behavior.[13] This means that the excitation and ionization of the plasma species are due to electron impacts. According to Table II, the initial energy level (E_k) of the O II lines observed in this spectrum are about 25 eV above the O II ground state. This implies that the energy distribution of

TABLE I. Emission lines λ and their transition energy levels $E_k \rightarrow E_l$ of the Ar I, Ar II, Hf I, and Hf II detected unambiguously in the optical spectrum of an Ar discharge.

	λ (nm)	E_l (eV)	E_k (eV)
Ar I	415.9	11.5	14.5
	419.1	11.5	14.5
	419.8	11.6	14.6
	420.1	11.5	13.8
	425.9	11.8	14.7
	426.6	11.6	14.5
	430.0	11.6	14.5
Ar II	372.9	16.6	20.0
	427.8	18.5	21.4
	434.8	16.6	19.5
	461.0	18.5	21.1
	472.7	17.1	19.8
	476.5	17.3	19.9
	480.6	16.6	19.2
	488.0	17.1	19.7
Hf I	368.2	0.0	3.4
	417.4	0.3	3.3
Hf II	264.1	1.0	5.8
	277.3	0.8	5.3
	313.5	0.4	4.3
	325.4	0.4	4.2
	340.0	0.0	3.6
	409.3	0.5	3.5

TABLE II. Emission lines λ and their energy levels $E_k \rightarrow E_l$ of the O I and O II detected unambiguously in the optical spectrum of an O_2 discharge.

	λ (nm)	E_l (eV)	E_k (eV)
O I	394.7	9.2	12.3
	436.8	9.5	12.4
	532.9	10.7	13.1
O II	391.2	25.7	28.8
	397.3	23.4	26.6
	407.6	28.7	25.7
	441.5	23.4	26.3
	464.2	23.0	25.7

showed a high chemical activation of the O atoms through the efficient dissociation of the O_2 molecules. The small radius and high reactivity of the O radicals lead to a replacement of the nitrogen by oxygen in the top layers of the SiN buffer films. On the other hand, the bonding structure of the SiN buffer layer is preserved during HfO_2 deposition in pure Ar atmosphere. This is a promising result that will be further studied since the aim of the SiN is acting as a diffusion/reaction barrier.

the electrons in the glow discharge reaches values of at least 25 eV. This high energy can only be achieved by secondary electrons ejected from the target and accelerated by the effect of the field across the dark space. As the dissociation energy of the O_2 molecule is 5.1 eV,[13] an efficient dissociation of the O_2 molecules is obtained by electron impact, leading to a high density of highly reactive O radicals, with higher diffusivity than the O_2 molecules. These radicals diffuse into the SiN layer forming Si–O bonds, and resulting in the release of the nitrogen of the first monolayers of the SiN buffer, as observed by FTIR and TEM.

In conclusion, we have studied the structural modifications of the SiN buffer layer on silicon induced by HfO_2 sputtering in Ar or O_2 atmospheres. When the HfO_2 is deposited with pure O_2, the SiN top layers oxidize, thus Si–O bonds are detected. This result has been explained by the analysis of the emission lines of the glow discharge, which

[1] M. Cho, J. Park, H. B. Park, C. S. Hwang, J. Jeong, K. S. Hyun, Y. Kim, C. Oh, and H. Kang, Appl. Phys. Lett. **81**, 3630 (2002).
[2] P. D. Kirsch, C. S. Kang, J. Lozano, J. C. Lee, and J. G. Ekerdt, J. Appl. Phys. **91**, 4353 (2002).
[3] M. Toledano-Luque, E. San Andrés, J. Olea, A. del Prado, I. Mártil, W. Bohne, J. Röhrich, and E. Strub, Mater. Sci. Semicond. Process. **9**, 1020 (2006).
[4] M. L. Lucía, J. L. Hernández-Rojas, J. Santamaría, I. Mártil, G. González-Díaz, and F. Sánchez-Quesada, Appl. Phys. Lett. **61**, 231 (1992).
[5] E. San Andrés, M. Toledano-Luque, A. del Prado, M. A. Navacerrada, I. Mártil, G. González-Díaz, W. Bohne, J. Röhrich, and E. Strub, J. Vac. Sci. Technol. A **23**, 1523 (2005).
[6] A. del Prado, E. San Andrés, I. Mártil, G. González-Díaz, D. Bravo, F. J. López, W. Bohne, J. Röhrich, B. Selle, and F. L. Martínez, J. Appl. Phys. **93**, 8930 (2003).
[7] D. A. Neumayer and E. Cartier, J. Appl. Phys. **90**, 1801 (2001).
[8] D. V. Tsu, J. Vac. Sci. Technol. B **18**, 1796 (2000).
[9] G. Norlén, Phys. Scr. **8**, 249 (1973).
[10] W. F. Meggers, C. H. Corliss, and B. F. Scribner, Natl. Bur. Stand. Circ. (U. S.) **145**, 387 (1975).
[11] R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (Wiley, New York, 1976).
[12] V. Hodoroaba, E. Steers, V. Hoffmann, W. Unger, and K. Wetzig, J. Anal. At. Spectrom. **18**, 521 (2003).
[13] B. Chapman, *Glow Discharge Processes* (Wiley, New York, 1980).