Nitridation of Si by N₂ Electron Cyclotron Resonance Plasma and Integration with ScOₓ Deposition


Departamento Física Aplicada III (Electricidad y Electrónica), Universidad Complutense de Madrid, 28040 Madrid, Spain

Nitridation of silicon was achieved by exposure of silicon to N₂ electron cyclotron resonance plasma. The growth rate decreased as the nitridation time increased due to the growth process being limited by the diffusion of nitrogen through the growing SiNₓ layer. The thickness of the SiNₓ layer was about 1.5 nm for a nitridation time of 30 s, according to ellipsometry and transmission electron microscopy measurements. Additionally, scandium oxide (ScOₓ) films were deposited by high pressure sputtering on top of the nitrided silicon, as well as reference un-nitrided silicon, to study the influence of the nitridation process on the interface properties. The silicon nitride layer is efficient in preventing the growth of interfacial silicon oxide. The minimum of the density of interface traps (D_it,min) for SiO/suboxide/SiNₓ/Si structures with 30 s nitridation was around 2 x 10¹⁴ cm⁻² eV⁻¹, indicating an improvement with respect to the ScOₓ deposition on un-nitrided silicon with D_it,min of about 1.2 x 10¹⁵ cm⁻² eV⁻¹. The best interface quality was obtained for the shortest nitridation time of 30 s. Finally, it was observed that the nitridation process greatly inhibits interface reaction during rapid thermal annealing at 1000°C.

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Logic technologies for the 32 nm generation have also been reported. However, research to further improve the properties or to find new high-k dielectrics is still required.

One subject of great concern is the control of the interface between the high-k dielectric and the substrate to prevent the growth of an undesired silicon oxide interface layer during the deposition of the high-k dielectric or during postdeposition annealing. The presence of such a low-k interface layer places a limit on the equivalent oxide thickness of the gate insulator that can be achieved. Additionally, when this silicon oxide grows in an uncontrolled way, it may lead to high densities of interface traps.

The incorporation of nitrogen into the interface, therefore forming a silicon nitride or silicon oxynitride layer, and its influence on the properties of gate structures using high-k dielectrics have been reported by many authors. The nitridation of silicon can be achieved by thermal processing in NO or NH₃ atmospheres or by different plasma techniques, such as NH₃/N₂ and N₂O/N₂ plasmas, N₂ remote plasma, a Xe/NH₃ microwave plasma, or N₂ plasma obtained by the low energy electron impact method. In these works, the leakage current is observed with respect to un-nitrided substrates. The presence of N also inhibits the formation of interfacial silicate during the growth of HfO₂. Additionally, a sufficiently high N concentration prevents thickness increase in the interfacial layer due to a reaction between Si and HfO₂ during postmetallization annealing. Higher densities of interface traps have been reported for NH₃-plasma-treated substrates with respect to N₂O-treated ones due to H-related traps. Low densities of interface traps (about 5 x 10¹⁰ eV⁻¹ cm⁻²) were observed for the Xe/NH₃ microwave plasma-treated substrates after deposition of SiO₂ to fabricate MOS devices, but in this work, structures using a high-k dielectric were not reported.

The effect of a SiNx interface layer grown by the electron cyclotron resonance (ECR) plasma technique, using N₂ and SiH₄ as precursors before deposition of HfO₂ by high pressure sputtering, has been reported by our group. It was observed that this layer prevents the growth of interfacial SiO₂ during the sputtering of HfO₂, and densities of interface traps of about 3 x 10¹⁴ eV⁻¹ cm⁻² were obtained. However, the presence of H limits the thermal stability of SiNₓ.

Most of the research concerning the nitridation of the Si substrate is focused on the interaction with gate structures based on hafnium oxide, which is the high-k material involved in the present 32 nm technologies. However, interest in compound high-k dielectrics involving scandium and oxygen, such as GdScO₃ or DyScO₃, has arisen due to their higher dielectric constant when compared to HfO₂ and high thermal stability. In addition to high performance logic applications, these materials are of interest as blocking oxides in floating gate and charge trapping flash memories. The effect of the nitridation of silicon using scandium oxide or a rare-earth scandate as high-k material has not yet been addressed.

The first goal of this work is to study the nitridation of silicon by exposing the substrates to N₂ ECR plasma. This technique is characterized by a high ionization efficiency. Therefore, it is expected to obtain a high N concentration in the nitrided layer. This is required for its effectiveness as a barrier against interface reactions. Additionally, by using N₂ to generate the plasma, no other elements such as hydrogen are intentionally introduced in the plasma atmosphere.

In the second part of the paper, the nitridation process is integrated with the deposition of scandium oxide by sputtering of a Sc₂O₃ target. Therefore, the capability of the nitrided layer to prevent the growth of interfacial silicon oxide is tested in an atmosphere containing oxygen. Additionally, the influence of nitridation on the interface properties is analyzed by comparing the deposition of ScOₓ in both nitrided and un-nitrided substrates. Finally, the effect of rapid thermal annealing processes is studied.

Experimental

Two types of silicon substrates were used in this work. For samples of series A, n-type (111) silicon substrates polished on both sides, with a resistivity of 200 Ω cm, were used. These substrates were mainly intended for absorption measurements. For samples of series B, the substrates were n-type (100) silicon with a resistivity of 5–20 Ω cm. These low resistivity substrates were used for the fabrication of MOS devices for electrical characterization. High resistivity (100) substrates were also used for Fourier transform infrared (FTIR) characterization of samples of series B. Results for both types of substrates were compared.

The substrates were cleaned by a standard RCA process, followed by...
lowed by a dip in 1:50 diluted HF for 30 s to remove the native oxide. This last step was performed immediately before loading the substrates into the deposition chamber, in N2 atmosphere, without exposing silicon to air.

The nitridation processes were performed using an ECR reactor model AX4500 (Astrum) attached to a stainless steel chamber. Details of the deposition system can be found in Ref. 25. Background pressure before the nitridation was about 6 × 10−12 mbar. A flow of 10.5 sccm of 99.9995% purity N2 was used in all the processes, corresponding to a pressure of 9 × 10−4 mbar. Substrate temperature was 200°C and microwave power was 100 W. These pressure and power conditions are known to achieve an efficient activation of N2 when SiNx is deposited from N2 and SiH4 gas mixtures.26 Nitridation time was varied between 30 and 3600 s to study the growth kinetics of SiNx.

To study the behavior of the nitried silicon upon deposition of scandium oxide (Sc2O3) and its effects on the interface, Sc2O3/SiN/Si stacks were fabricated. Deposition of Sc2O3 on bare Si substrates was also performed for comparison. The Sc2O3 films were deposited by a high pressure sputtering system, which is described in Ref. 27. A Sc2O3 target with a nominal purity of 99.95% was used. Background pressure was 2 × 10−6 mbar. For plasma generation, a flow of 6.4 sccm of 99.9995% purity Ar was introduced into the chamber. During the deposition, substrate temperature was 200°C, chamber pressure was 0.5 mbar, and the radio-frequency power was 40 W.

The bonding structure of the films was analyzed by FTIR spectroscopy using a Nicolet Magna-IR 750 series II spectrometer working in transmission mode at normal incidence. The spectrum of each silicon substrate was measured before the nitridation process. Then, the very same samples were measured after the nitridation process and once again after the deposition of Sc2O3. Therefore, the SiN layer spectrum was obtained by subtracting the Si spectrum from the total SiN/Si spectrum. Likewise, any changes in the nitried layer after deposition of Sc2O3 can be observed by comparing the Sc2O3/SiN/Si stack spectrum with the SiN/Si spectrum. The thickness and refractive index of the SiN layers were measured by ellipsometry using a Nanofilm EP3-SW ellipsometer working at λ = 532 nm, with incidence and detection angles set at 70°. The structure and thickness of the samples were also analyzed by transmission electron microscopy (TEM) using a JEOL-JEM-2000FX microscope operating at 200 keV and by high resolution transmission electron microscopy (HRTEM) using a JEOL-JEM-4000EX microscope operating at 400 keV. For these measurements, the samples were cut into two pieces and glued together face to face using G1 epoxy.

MOS devices were fabricated for electrical characterization by electron-beam evaporation of aluminum contacts on the Sc2O3/SiN/Si and Sc2O3/Si structures. Postmetallization annealing in forming gas atmosphere at 300°C for 20 min was performed. The density of interface traps was obtained from simultaneous quasi-static and high frequency capacitance–voltage (C–V) measurements performed with a Keithley model 82 system. The thickness of the Sc2O3 layer in these devices was about 30 nm, which ensured leakage currents low enough to perform the quasi-static measurements.

Rapid thermal annealing processes were performed in a Modular Process Technology furnace (model RTP-600) in dry N2 atmosphere at 1000°C for 30 s. Changes in the structure of bonds were analyzed by FTIR measurements performed before and after annealing.

Results and Discussion

SiN/Si structures.— Figure 1 shows the absorbance IR spectra of characteristic samples of series A, subjected to different times of N3 plasma nitridation, after removing the Si substrate signal and without performing any baseline correction. The spectra have been shifted in the absorbance axis for clarity. For a nitridation time of 3600 s, a broad absorption band with its maximum located around 860 cm−1 is clearly observed. This band is characteristic of silicon nitride,26 indicating that the nitridation of silicon has been achieved. As the nitridation time decreases, the intensity of this band decreases, indicating that the thickness of the SiN layer decreases as expected. For deposition times below 1800 s, the location of the maximum of the band can be clearly determined, extending to the 860–900 cm−1 range. In a previous work, we correlated the position of the main absorption band with the composition of SiONx films deposited using the same reactant.26 The presence of O in the deposited films was detected even when O was unintentionally introduced in the plasma atmosphere. Additionally, a maximum of the Si–O/Si–N stretching band at 900 cm−1 was found for a composition characterized by the ratio of 38% is obtained. This provides a rough estimation of the maximum O concentration present in our films. Therefore, it is concluded that the nitridation process leads to a silicon nitride or oxynitride film with a high N concentration. In the following, the nitried layer is addressed as SiNx, even though O is present in this layer. An [O]/[N] ratio of about 40% was reported by Higuchi et al.15 after nitridation in NH3 microwave plasma with increasing O concentration near the surface of the nitried layer. A higher [O]/[N] ratio of about 54% was reported by Kobayashi et al. for nitridation using N2 plasma obtained by the low energy electron impact method.26

The valleylike feature observed around 1060 cm−1 is related to the native oxide. The native oxide is removed before the nitridation process. However, when measuring the substrate signal, the native oxide is present because the substrates are exposed to the atmosphere. (In fact, the HF dip step was performed after measuring the spectra of the substrates.) Therefore, what we call “the substrate signal” includes the absorption from the substrate as well as the native oxide absorption. So, when the substrate spectrum is subtracted from the nitried sample spectrum, the native oxide signal is also subtracted. Because the native oxide is not present in the nitried sample, it appears as a negative value.

The thickness of the SiNx layers obtained from ellipsometry is shown in Fig. 2 as a function of nitridation time for samples A and B. The line corresponds to the fit of the data of series A, as explained below. First of all, it is observed that the growth of the silicon nitride does not depend on the silicon orientation for (100) and (111) silicon. This same result was reported for NH3 microwave plasma nitridation of (100) and (110) silicon.15 Therefore, in the following, our study is focused on the (100) substrates. Second, a clearly nonlinear behavior of the growth rate is observed. An em-

\text{Absorbance (relative units) vs Wave number (cm}^{-1})$

\text{Figure 1. Absorbance spectra for samples of series A, subjected to nitridation at different times.}
The diffusion of N through the growing SiN rate decreases. This result indicates that the nitridation is limited by previously described. As the nitridation time increases, the growth seconds. This relationship applies only for the nitridation conditions also reported for nitridation in NH3 plasma for times above 180 s.15 A similar behavior of thickness as a function of nitridation time was observed even for nitridation times as low as 30 s, which indicates that the initial nitridation of silicon is achieved in a very short time. A similar behavior of thickness as a function of nitridation time was also reported for nitridation in NH3 plasma for times above 180 s.15

The thickness obtained by TEM is consistent with the ellipsometry results within the uncertainty of the techniques. From the FTIR, ellipsometry, and TEM results, it is concluded that the nitridation of the substrate has been achieved, with control of the SiN thickness down to about 1.5 nm for a nitridation time of 30 s.

ScOx/SiN/Si and ScOx/Si stacks.—The spectra of the samples before and after ScOx deposition are shown in Fig. 5. Trace A corresponds to a SiN/Si structure for 600 s nitridation after removing the Si substrate signal, like the spectra shown in Fig. 1. The sharp feature appearing at 670 cm\(^{-1}\) is related to CO\(_2\),29 which is present in the background atmosphere and is sometimes observed in the measurements. Because this band does not interfere with the Si–O or Si–N stretching vibrations studied in this work, the spectrometer was not purged. Trace B shows the spectrum of the very same sample after deposition of the ScO\(_x\) layer. Finally, trace C shows the reference spectra of a ScO\(_x\) film deposited on an un-nitrided silicon substrate.

We first discuss the influence of ScO\(_x\) deposition on the SiN layer. It is observed that after deposition of the ScO\(_x\) film, the SiN band previously described is still present, indicating that the SiN, although a quantitative evaluation of the composition was not possible. For very short nitridation times, the silicon nitride layer is not clearly observed. Figure 4 shows an HRTEM image for a sample of series B nitrided for 30 s. A layer of about 1 nm can be detected between the epoxy and the silicon substrate, which we identify as SiN\(_x\). The thickness obtained by TEM is consistent with the ellipsometry results within the uncertainty of the techniques.

Figure 5. Absorbance spectra after removing Si substrate signal for (a) a SiN/Si structure with 600 s nitridation, (b) the resulting ScO\(_x\)/SiN/Si structure after ScO\(_x\) deposition, and (c) a reference ScO\(_x\)/Si structure.

Figure 4. Cross-sectional HRTEM picture for a sample of series B subjected to 30 s nitridation.

Figure 3. Cross-sectional TEM picture for a sample of series B subjected to 120 s nitridation.

Figure 2. Thickness of the SiN layers obtained by ellipsometry as a function of nitridation time for samples of series A and B using different types of substrates.
layer remains after this process. However, a broadening of the band at the higher wavenumber zone is also observed. This is shown in detail in Fig. 6, where the difference spectrum between the ScO$_x$/SiN$_x$/Si and SiN$_x$/Si structures is shown as trace A. The result for a sample with a nitridation process of 30 s is also shown as trace B. The narrow feature appearing at about 840 cm$^{-1}$ is attributed to an imperfect correction of the substrate absorption. A weak band located around 1000 cm$^{-1}$ becomes apparent. This wavenumber is well below the characteristic value for SiO$_2$ (about 1070 cm$^{-1}$). Also, this band is observed for both nitridation times of 30 and 600 s, being slightly more apparent for the longer nitridation time, which means the thicker SiN$_x$ layer. The substitution of a silicon atom by a heavier one in a Si–O–Si group shifts the vibration frequency to lower values.

Another subject of our study is the comparison of the interface formed when the Si substrate is subjected to nitridation and when ScO$_x$ is directly deposited on un-nitrided Si. The corresponding absorption spectra are shown in Fig. 5 (traces B and C, respectively). A comparison of the spectrum of the ScO$_x$/Si reference structure and the ScO$_x$/SiN$_x$/Si stacks is shown in Fig. 7. The line shown is the spectrum difference obtained by subtracting the ScO$_x$/SiN$_x$/Si signal from the ScO$_x$/Si signal. The result is shown for nitridation times of 600 and 30 s. The valley feature located around 910 cm$^{-1}$ corresponds to the nitridated layer, which is not present in the ScO$_x$ structures. A characteristic silicon oxide absorption band located at about 1060 cm$^{-1}$ is also observed. This indicates that SiO$_2$ is formed when ScO$_x$ is directly deposited on un-nitrided silicon, which is not present when ScO$_x$ is deposited on nitrided Si. The intensity of this band is the same for nitridation times of 30 and 600 s. Therefore, it is concluded that the nitridation process is efficient in preventing the growth of interfacial SiO$_2$, even for nitridation times as low as 30 s.

The structure of the ScO$_x$/Si and ScO$_x$/SiN$_x$/Si samples was analyzed by TEM. Figure 8 shows the TEM images of these structures. For the deposition of ScO$_x$ on un-nitrided silicon, an interface layer of about 1.7 nm is observed. This interface layer is attributed to the formation of SiO$_x$, which agrees with the FTIR spectroscopy results.

For the ScO$_x$/SiN$_x$/Si structure, an interface layer is also observed. The thickness of this interface layer increases with respect to the SiN$_x$ nitrided layer before deposition of ScO$_x$. This may be explained by the formation of Sc–O–Si groups or by the formation of new Si–O bonds at the nitrided layer, as previously suggested.

To study the interface electrical characteristics, the energy distribution (trap energy $E_T$ with respect to the conduction band edge $E_C$) of the density of interface traps was obtained from simultaneous quasi-static and high frequency C–V measurements. The result is shown in Fig. 9 for the reference ScO$_x$/Si structure and ScO$_x$/SiN$_x$/Si stack structures with nitridation times of 600 and 30 s. A poor quality interface, with a minimum of the density of traps ($D_{n,\min}$) of about $1.2 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$, was obtained when ScO$_x$ is deposited on an un-nitrided substrate. This low quality is determined by the SiO$_2$ interface that is formed in this process. When the substrates are subjected to a nitridation process before the deposition of ScO$_x$, the interface quality greatly improves, reducing the density of interface traps. For these devices, the nitridation of the substrate prevents the formation of the low quality SiO$_2$. As shown in Fig. 9, the improvement is greater for the short nitridation time of 30 s, for which the minimum of the density of interface traps is about $2 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$.

Finally, the influence of nitridation during postdeposition rapid thermal annealing at 1000$^\circ$C was studied. Figure 10 shows the spectrum difference between the annealed samples and the as-deposited ones for ScO$_x$/Si and ScO$_x$/SiN$_x$/Si structures with nitridation times of 30 and 600 s. The characteristic silicon oxide band at 1072 cm$^{-1}$ is observed for ScO$_x$ deposited on an un-nitrided substrate.

![Figure 6](image6.png)  
**Figure 6.** Spectrum difference between ScO$_x$/SiN$_x$/Si structures and SiN$_x$/Si structures for nitridation times of (a) 600 and (b) 30 s.

![Figure 7](image7.png)  
**Figure 7.** Spectrum difference between ScO$_x$/Si structures and ScO$_x$/SiN$_x$/Si structures for nitridation times of (a) 600 and (b) 30 s.

![Figure 8](image8.png)  
**Figure 8.** Cross-sectional TEM images of (a) a ScO$_x$/Si structure and (b) a ScO$_x$/SiN$_x$/Si structure with 30 s nitridation time.
indicates that after 1000°C annealing, an increase in the silicon oxide layer takes place. For SiOₓ deposited on the nitrided substrates, a band with lower intensity and shifted to lower wavenumbers is observed. This indicates that interface reaction to form silicon oxide is greatly inhibited by the nitridation process even for nitridation times as low as 30 s.

Conclusions

Nitridation of (111) and (100) silicon substrates was performed by exposure of the substrates to Nₓ ECR plasma. Silicon oxynitride layers were obtained with high N concentrations. The thickness of the nitrided layer can be controlled by adjusting the nitridation time. Values of about 1.5 nm have been obtained for nitridation times of 30 s, independent of the substrate orientation. As nitridation time increases, growth rate exponentially decreases due to it being limited by N diffusion through the growing layer.

The nitried layer is efficient in preventing the formation of a SiOₓ interface layer during the deposition of SiOₓ by sputtering. The minimum of the density of interface traps in SiOₓ/SiNx/Si structures with 30 s nitridation is about 2 × 10¹³ cm⁻² eV⁻¹, which means great improvement with respect to 1.2 × 10¹³ cm⁻² eV⁻¹ obtained when SiOₓ is deposited on an un-nitried substrate. An increase in the thickness of the interface layer after SiOₓ deposition on nitrided substrates has also been observed, which may be related to the formation of Sc–O–Si groups or new Si-O bonds from Si present in the nitried layer. Finally, interface reaction between ScOₓ and Si to form SiOₓ after rapid thermal annealing at 1000°C is greatly inhibited by the nitridation process.

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