Characterization of Very Thin Thermally Nitrided-SiO₂/Si Interface Properties with Conductance and Hot Electron Injection Measurement

Z.H. Liu, Y.C. Cheng and H. Wong

Department of Electrical and Electronic Engineering
University of Hong Kong, Pokfulam Road, Hong Kong

The electrical properties of thermally nitrided-oxide/silicon interface are investigated by conductance and hot electron injection techniques. Results show that the interface properties are strongly dependent on the nitridation conditions. Generally, a nitridation process significantly increases the hole capture cross section, reduces the uniformity of surface potential, and enhances the strength of interface against hot electron bombardment. These results can be deduced from the process induced structural change of the nitrided films but not from the effects of the hydrogen and hydroxide radicals.

INTRODUCTION

Nitridation of oxide film is now receiving increasing attention and is regarded as a good gate material for ULSI application because of its properties of higher breakdown field and stronger irradiation resistance\(^1\)-\(^4\). Various nitridation processes and their corresponding kinetics have been studied extensively. However, the information about interface properties of nitrided-oxide is still inadequate. It is found that experiments on the nitrided-oxide/silicon interface were all on the quasistatic and high frequency capacitance-voltage(CV) methods\(^1\)-\(^5\). Similar to the case of silicon oxide, a more detailed exploration of the interface properties, including the trap capture cross section, capture time constant and the roughness of interface is adopted to characterize the nitrided-oxide/silicon interface. In this work, we will report the first investigation on trap capture cross section of the ultra thin (10-20nm) nitrided-SiO₂/Si interface by conductance method, and interface traps properties by hot electron injection technique which is usually used for studying the bulk trap properties\(^6\)-\(^8\).

EXPERIMENTAL

The substrates used in this investigation were p-type \(<100>\) silicon wafers. For the conductance measurement, the resistivity of substrate was 3-5 ohm-cm, while for hot electron injection measurement, a resistivity of 0.3-0.4 ohm-cm was used to eliminate the edge effect\(^8\). Wafers were oxidized in an \(\text{O}_2\) partial pressure of 0.2 atm at 970°C, to a thickness of either 10 nm or 20 nm. Film thicknesses were measured by a Rudolph Research 43603 ellipsometer and verified by a CV measurement. The thermal nitridations were performed in a resistance furnace in an \(\text{NH}_3\) ambient of 1 atm at 970°C or 1050°C for 15-60 minutes. Lastly, aluminum was deposited on the surface of nitrided film and a 6.5x10\(^{-4}\)cm\(^2\) electrode was formed. No annealing was performed in order to preserve all features of the interface state inherent with the oxidation and nitridation processes.

Capacitance and conductance of a metal-insulator-semiconductor (MIS) capacitor were measured simultaneously using a two-phase lock-in amplifier. The interface state density (\(D_{it}\)), hole capture cross section (\(\sigma_P\)), and standard
deviation of surface potential fluctuations ($\sigma_s$) were evaluated by directly fitting the experimental conductance ($\sigma_p/\omega$) versus the angular frequency ($\omega$) curves to the theoretical ones. The high frequency (1MHz) CV and quasistatic CV curves were also measured in order to correct the error introduced by the serial resistance and to determine the fixed charge density $Q_{ox}$. A detailed description of the measuring procedures and devices is reported elsewhere.

RESULTS AND DISCUSSIONS

Figure 1 shows the interface states densities measured by conductance technique as a function of energy from midgap for various processing conditions. Results of quasistatic CV method are also given in the same figure for comparison. It can be seen that both conductance and quasistatic techniques give a similar result, i.e. the nitrided films have a higher interface state level than that of oxide. However, it seems that quasistatic technique always overestimates $D_{it}$. In addition, the conductance technique can generate either a more, or a less uniform distribution of $D_{it}$ over the accessible bandgap depending on the nitridation conditions. For the same samples, the results of hole capture cross section versus bandgap energy are given in Fig.2. Results suggest that the nitridation parameters have a strong correlation with the interface state density and also with the $\sigma_p$. For a given nitridation temperature, the longer the nitridation duration, the lower the $D_{it}$ and the larger $\sigma_p$ will be. A high nitridation temperature, unfortunately, will increase both $D_{it}$ and $\sigma_p$. Furthermore, a nitridation always increases the $\sigma_p$ as shown in Fig.2. This implies that the $\sigma_p$ depends more strongly on nitridation conditions than on those of $D_{it}$. Since nitridation usually introduces a large density of fixed charge, hydrogen(H) and hydroxide(HO) radicals may be responsible for the large, negative shift of

Fig.1 Interface state density versus energy from midgap by conductance (markers) and Quasistatic (lines) techniques.

Fig.2 Hole capture cross section versus energy from midgap. The samples are the same as those used in Fig.1.
V_{fb} and the generation of oxide charge (Q_{ox}), 1,3) as well as the high density of bulk traps6) induced during nitridation. More recently, studies on the compositional distribution show that nitridation seems unlikely to change the total amount of H in the bulk but does slightly increase the number of H-N bonds 11-12). In addition, it was suggested that a higher nitridation temperature would introduce lower concentration of hydrogen10). Therefore, if the incorporated H or HO radicals degrade the interface properties during nitridation, the higher nitridation temperature should lead to a decrease of the D_{it} and σ_{p} rather than an increase. Besides, it was reported that there is a strong correlation between the fixed charge accumulation and nitridation duration as well as the temperature1,2,4,5), but no obvious dependence of σ_{s} on the nitridation parameters was observed in our work. Because of the fact that the incorporated nitrogen in a nitrided film increases monotonically with reaction temperature and time,4-5,10-13) and due to the modification of the structure of SiO_{2}, especially at the interface to form Si_{2}N_{2}O and Si_{3}N_{4} in nitridation5,12,13) an interface strain may exist9). We therefore propose that the larger value of σ_{p} is most likely due to the interface strain from structural modification due to the larger cross-linking created by nitrogen.14)

Figure 3 demonstrates the effect of hot electron injection on the CV characteristics of an oxide and a nitrided-oxide. It indicates that for the same injection parameters, the C-V curves of the nitrided sample exhibit much less distortion than that of conventional oxide in spite of that a large shift of flat band voltage (V_{fb}) is observed for the nitrided sample. Since both charges in bulk trap and interface state can consequently lead to the shift of V_{fb}15), it is difficult to distinguish whether the shift is due to the interfacial charge or bulk trap charge. Fortunately, since the current-voltage (IV) characteristics of the MIS capacitor are insensitive to interface charges,16) we can use the IV curves to study the hot electron injection effects on the interface properties. These results are given in Fig.4, where the insert shows the V_{fb} shift as a function of injection time. Note that before injection, the conduction of nitrided oxide under low field (<5MV) is slightly enhanced as we previously reported,17) while at high field (>6MV) the nitrided-oxide possesses a much lower dynamic resistance r (r=\partial V/\partial I) than that of the oxide which can be explained by the high density of bulk trap in a nitrided oxide. Although the V_{fb} shift for nitrided oxide is about two times larger than that of oxide, the shift of IV curves along voltage axis for nitrided oxide is much

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure3}
\caption{C-V characteristics before and after hot electron injection for oxide (a) and nitrided oxide (b). The initial oxide thickness is 20nm. The injection DC current is 2x10^{-8}A and the frequency of injection signal is about 500 KHz.}
\end{figure}
smaller than that of oxide, especially at low field. At high field, as a result of new bulk traps generation, the dynamic resistance of nitrided oxide is further lowered. Because of the low injection field (5-6MV) for avalanche hot electron\(^8\), the large \(V_{fb}\) shift after injection should mainly be due to the high density of bulk trap for the nitrided oxide. In general, the hot electron induced generation of interface state for a nitrided oxide is more or less eliminated by the structural modification in comparison with a similar SiO\(_2\) film.

In summary, nitridation of silicon oxide will degrade the smoothness of the interface and the uniformity of surface potential. In addition, it can slightly increase the interface state density but significantly increase the hole capture cross section. The large capture cross section of nitrided oxide, which probably leads to the poor interface conditions of nitrided-SiO\(_2\)/Si interface, most likely results from the nitridation induced structural modification rather than from the effects of H and HO radicals. Above all, because of the longer endurance of hot electron bombardment, the nitrided film may become a good substitute for silicon oxide for small geometry devices requiring high reliability.

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REFERENCES