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Study of Penetrated Boron Concentration through Ultra-Thin Oxynitrided Gate Dielectrics

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This paper describes an extended model for estimation of penetrated boron from simple C-V measurement. This model, which is based on the assumption that only penetrated boron atoms within a Debye length of the interface contribute to the flatband voltage (V_{fb}) shift, is applied to a comparison of boron penetration through reoxidized-nitrided-oxide (ROXNOX) and N_2O oxynitride films. It is found that both the nitrogen content and the nitrogen profile are important in determining the amount of boron penetration.

1 Introduction

For the realization of low-power sub-quarter μm CMOS devices, surface channel PMOS structures with boron-doped P^+ polysilicon gates are needed. In the thermal cycles after gate stack fabrication, boron atoms can easily diffuse through the gate dielectric and cause large threshold voltage shifts. Recently, oxynitrides have been studied by many researchers for their benefit of preventing boron penetration. However quantitative techniques are still needed to evaluate boron penetration electrically. In the present work, we extend the boron penetration model from previous work [1] and use this model to understand the different penetration behavior between reoxidized-nitrided-oxide (ROXNOX) and N_2O oxynitride films.

2 Experimental

MOS capacitors were fabricated with 5nm-thick 950°C dry oxides grown on n-type and p-type substrates doped to $1 \times 10^{15}cm^{-2}$. The gate electrode was prepared from undoped 150nm-thick polysilicon implanted with B at 10 KeV and a dose of $5 \times 10^{15}cm^{-2}$. Subsequent N_2 annealing was carried out at 900, 950 and 1000°C for 1 hour. Corresponding samples were prepared for spreading resistance profiling (SRP) analysis, allowing a quantitative comparison of the interfacial boron concentration determined from V_{fb} shifts and from SRP.

For investigation of oxynitrides, MOS capacitors were prepared using a PMOS fabrication process, with an n-well surface doping level of $5 \times 10^{17}cm^{-3}$. Four kinds of gate dielectrics were used, with effective gate oxide thicknesses of 4.5nm to 8nm: ROXNOX (750°C wet base-oxide / nitridation by RTP at 850 to 950°C in NH_3/ re-oxidation by RTO at 1050 to 1150°C), 850 to 1050°C N_2O furnace-annealed oxynitride with 5nm-thick 750°C wet base-oxide, 850°C N_2O furnace-annealed oxynitride without a base-oxide, and a reference 750°C wet oxide film. The gate polysilicon was BF_2-implanted at 30KeV and a dose of $3 \times 10^{15}cm^{-2}$, followed by a 30 minute anneal in N_2 at 850°C. Total nitrogen content in the oxynitride films (C_N) was measured by nuclear reaction analysis $(NRA)^2$, which has a detection limit of about $6.0 \times 10^{13}cm^{-2}$. The nitrogen depth profiles were estimated by the etching-rate ratio of $SiON/SiO_2$ during step etching in diluted HF solution. The electrical characteristics of both sets of MOS capacitors were obtained by 100 kHz C-V measurements on 1×10^{-3} cm^2 capacitors.

3 Results and Discussion

3.1 Boron penetration model

The two layer diffusion model[3] has been previously applied to the phenomena of the boron penetration in the gate dielectric and substrate structure[1], shown schematically in Fig.1. The boron concentration at depth x in the substrate, $C(x)$, is expressed as:

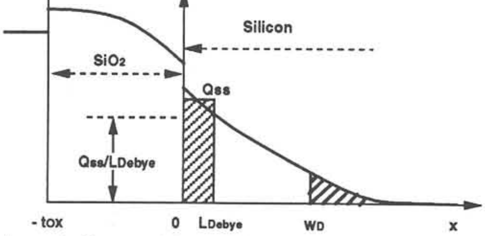

Fig.1. Schematic diagram of the models for estimation of penetrated boron atoms. Presented model assumes that penetrated boron atoms within Debye length cause a flat band shift. Qss was calculated from the following relation, Qss = Cox x ΔV fb. Qss/LDebye value is considered to be the average interfacial boron concentration within Debye length. Although boron atoms outside of a Debye length are not measured, the previous model included them in its analysis.

$$C(x) = m(1-\alpha)C_o \cdot \mathrm{erfc}\left(\frac{t_{ox}+\gamma x}{2\sqrt{D_1 t}}\right) \qquad (1)$$

where $\alpha = (m-\gamma)/(m+\gamma), \gamma = \sqrt{D_1/D_2}$, $D1$ and $D2$ are the diffusivity of boron in the gate dielectric and the substrate respectively, m is the segregation coefficient at the Si/SiO_2 interface and C_o is the boron concentration in the gate polysilicon. In previous work, the boron penetration was modeled by integrating $C(x)$ infinitely deep into the substrate.

We propose a new value C_{ave} (cm^{-3}), which is the interfacial boron concentration averaged over the Debye length (L_{Debye}).

$$L_{Debye} = \sqrt{\frac{\varepsilon_s kT}{q^2 N_{sub}}} \qquad (2)$$

$$C_{ave} \equiv \frac{1}{L_{Debye}} \int_0^{L_{Debye}} C(x)dx \qquad (3)$$

C_{ave} is experimentally evaluated as Q_{ss}/L_{Debye}, where $Q_{ss} = C_{ox} \times \Delta V_{fb}$. This approach was tested using the simple cases of dry oxides on p-type and n-type substrates with boron-implanted gate polysilicon. Fig.2 shows the measured HF C-V curves of the post-annealed samples. For p-substrate samples shown in Fig.2(a), the minimum capacitance (C_{min}) increases and the inversion-to-accumulation slope decreases with higher annealing temperature. This can be explained by an increase in penetrated boron, which simply increases the p-type doping concentration at the surface. On the other hand, the n-substrate samples shown in Fig.2(b) have large V_{fb} shifts, due to the buried layers created by the penetrated boron. In these samples, the penetrated boron has a negligible effect on C_{min}, as long as the penetration depth is less than the maximum depletion-layer thickness.

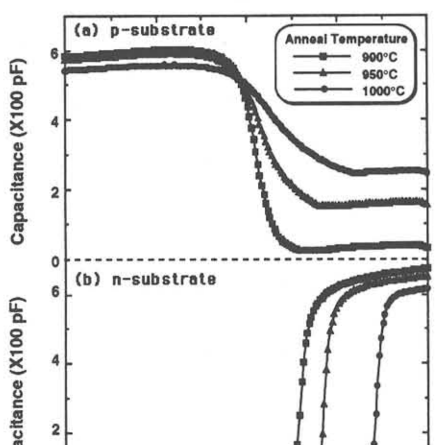

Fig.2. High-frequency curves of p- **(a)** and n-**(b)** substrates. Gate dielectric films were 5nm dry oxide and boron ion implantation into poly-Si gate electrode was performed. Subsequent N2 annealings were carried out at 900, 950 and1000°C for 1 hour. As annealing temperature increases, Cmin increases for p-substrate, while a Vfb shift is seen in n-substrate.

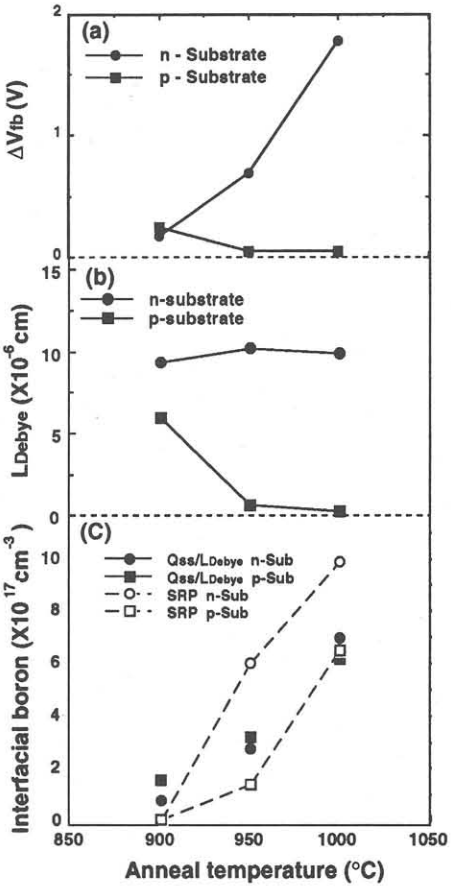

Fig.3 (a). Vfb vs. anneal temperature. Vfb decreases slightly with increasing anneal temperature in p-substrate due to a changing substrate doping. Samples are the same as in Fig. 2.
(b). Debye length vs. anneal temperature as calculated from Cmin.
(C). Interfacial boron concentration vs. anneal temperature. Solid marks represent Qss/LDebye values. Debye length was calculated from C-V curves. Qss/LDebye value increases with anneal temperature in both n- and p-substrate samples. Open marks represent average interfacial boron concentration estimated from SRP measurement. Note that the buried channel structures are formed in 950 and 1000°C annealed samples in n-substrates.

Extracted values of ΔV_{fb} and L_{Debye} are shown for these samples in Fig.3(a) and Fig.3(b) respectively. The correlation of estimated Q_{ss}/L_{Debye} with the boron concentration obtained by SRP was confirmed, as shown in Fig.3(c). Good agreement is found between the SRP and C-V results, despite the simplifying assumption of a uniform substrate profile in extracting V_{fb}.

3.2 Comparison of oxynitrides

We used this approach to characterize and compare boron penetration in various oxynitride films. As shown in Fig.4, the flatband voltage shift due to boron penetration is related to the nitrogen content in the films but also depends on the details of the gate-dielectric process. We consider the cases of ROXNOX and N_2O oxynitride with base-oxide. Even with the same C_N of $6 \times 10^{14} cm^{-2}$, the N_2O film has a smaller V_{fb} shift than the ROXNOX film. This difference can be attributed to differences in the nitrogen profiles, which were were investigated by step etching, shown in Fig.5. The ROXNOX film has a sharp nitrogen peak in the center of the dielectric, while the N_2O film has broad

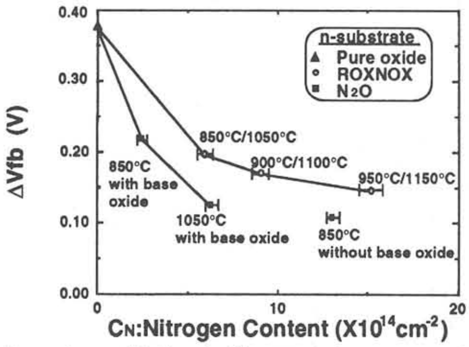

Fig.4. Dependence of flat band shift on total nitrogen atoms in pure oxide, ROXNOX and N2O oxynitrided samples. These films were formed on n-substrates. Total thickness of all the samples was 7nm. Nitridation temperature was varied to adjust the nitrogen content.. All the samples were annealed at 850°C for 30minutes.Total amount of nitrogen was measured by nuclear reaction analysis.

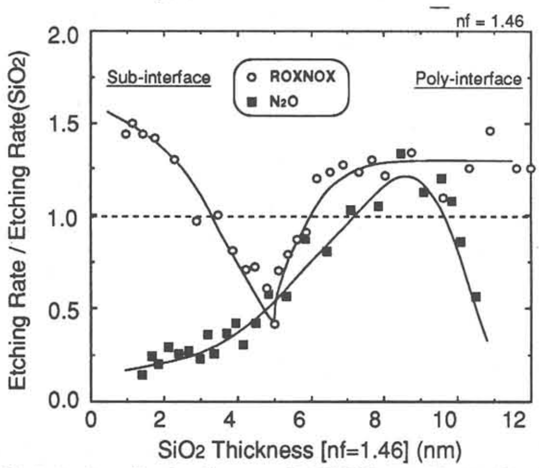

Fig.5. Depth profile of etching rate of ROXNOX (850°C/ 1050°C) and N2O (1050°C with 5nm base oxide) samples. Etching rate is normalized to the etching rate of thermal SiO2. Nitrogen atoms can be detected by small etching rate. The thickness of the samples was about 11nm.

peaks at both interfaces. This suggests that nitrogen at the interface is most effective at blocking boron diffusion.

Our model allows the boron diffusivity in the gate dielectric to be estimated from interfacial boron vs. dielectric thicknesses results. For the case of a pure oxide film, shown in Fig.6, the diffusivity was extracted as $2.3 \times 10^{-17} cm^2 \cdot sec^{-1}$, which is comparable to the previous work. In the case of N_2O oxynitride without a base-oxide, the diffusivity was extracted as $1.7 \times 10^{-17} cm^2 \cdot sec^{-1}$. For the N_2O oxynitride with a base oxide (not shown), the penetrated boron at 7 nm was close to the detection limit of $10^{16} cm^{-3}$, and no diffusivity could be extracted.

Surprisingly, boron penetration through the ROXNOX film is significant, but shows no thickness dependence, so diffusivity could not be calculated using the model based on Fig.1. The ROXNOX nitrogen profile in Fig.5 indicates that the nitrogen is piled up in the film about 5 nm from the Si/SiO_2 interface. This nitrogen layer is believed to function as a boron blockade, with a lower diffusivity than the regions of pure oxide at both interfaces. This result suggests that oxynitride gate dielectrics would be better modeled as multi-layer films, with each layer having a different diffusivity. For the case of ROXNOX, the total boron

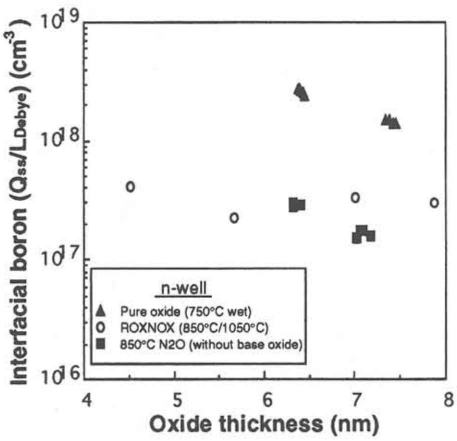

Fig.6. Average interfacial boron concentration of pure oxide, ROXNOX (850°C/1050°C) and N2O (850°C without base oxide) samples. These films were formed on n-well. All the samples were annealed at 850°C for 30 minutes in N2 ambient.

penetration may be limited by the boron blocking efficiency of the center nitrogen-rich layer, and by the thickness of the SiO_2 layer adjacent to the substrate. As long as these layers are not modified by the initial oxidation, the boron penetration should not depend on dielectric thickness. Overall, it is clear that in engineering oxynitrides to block boron penetration, both the total nitrogen content and the nitrogen profile within the dielectric must be taken into account.

4 Conclusions

In summary, we have extended a previous model of boron diffusion through gate dielectrics, and used SRP to confirm its validity. This model enables quantitative study of boron penetration with simple C-V measurements and is shown to be useful in understanding boron blocking in different oxynitride films. We have demonstrated that both the nitrogen content and the nitrogen profile are important in determining the degree of boron penetration.

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