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# The Relation between Dielectric Constant and Film Composition of Ultra-Thin Silicon Oxynitride Films: Experimental Evaluation and Analysis of Nonlinearity

Naoki Yasuda, Kouichi Muraoka, Masahiro Koike and Hideki Satake
Advanced LSI Technology Laboratory, Toshiba Corporation
8, Shinsugita-cho, Isogo-ku, Yokohama 235-8522, Japan
Phone: +81-45-770-3693, Fax: +81-45-770-3578, E-mail: n-yasuda@amc.toshiba.co.jp

## 1. Introduction

In near-future CMOS technology nodes, silicon oxynitride with high nitrogen concentration is considered as a strong candidate for gate dielectrics [1]. In order to predict device characteristics such as the tunneling current across the gate dielectrics, it is necessary to study the basic properties of ultra-thin silicon oxynitride in a wide range of film composition (i.e. from pure $SiO_2$ to pure $Si_3N_4$). In this paper we report the experimental determination of dielectric constant ($\varepsilon$) and film composition (x in $(SiO_2)_x(Si_3N_4)_{1-x}$) in ultra-thin, uniform silicon oxynitride films. We have found the presence of nonlinearity in the $\varepsilon$-x relation, and attribute it to the difference in minimum atomic units for dielectric constant and film composition. We conclude that a tetrahedron around Si should be used as the minimum unit for dielectric constant. Additionally, we suggest that uniform nitrogen profile is effective in reducing direct tunneling current, owing to the nonlinear $\varepsilon$-x relation.

## 2. Experimental

We used plasma-enhanced CVD oxynitride films to assure uniformity in nitrogen and oxygen depth profiles. The oxynitride films were deposited at 500°C by introducing $SiH_4$ (20 sccm), $O_2$ (0 – 0.1 Torr), and the radicals of $N_2$ generated by microwave plasma excitation. The samples were then transferred into an in-situ XPS analysis chamber, and film composition was characterized. MIS capacitors with an $n^+$poly-Si gate were fabricated out of these samples. The physical thickness of the oxynitride films was determined by cross-sectional TEM (5-6 nm), while the effective thickness $T_{eff}$ (3-4nm) was derived from C-V measurements. For accurate determination of $T_{eff}$, the capacitances of substrate accumulation and gate depletion were carefully removed with a procedure similar to the one described in Ref.[2].

## 3. Results and Discussion

In Fig. 1 we show the composition of silicon oxynitride films in ternary composition diagram. The composition falls on the tie-line between $SiO_2$ and $Si_3N_4$, meaning that the minimum units for film composition are $SiO_2$ and $Si_3N_4$. It also indicates constant coordination numbers of 2, 3 and 4 for O, N and Si, respectively (2[O] + 3[N] = 4[Si]). In Fig.2 we show the relation between dielectric constant ($\varepsilon$) and film composition (x) for the ultra-thin oxynitride films, together with the $\varepsilon$–x relation in much thicker films [3,4]. We conclude that the dielectric constant of ultra-thin, uniform oxynitride films is the same as that of the thick films. The nonlinear $\varepsilon$–x relation in silicon oxynitride is empirically described with $\varepsilon = \varepsilon(SiO_2)\ r + \varepsilon(Si_3N_4)\ (1-r)$ where $r = [Si\text{-}O] / ([Si\text{-}O] + [Si\text{-}N]) = x / (3 - 2x)$. In this expression, [Si-O] and [Si-N] are the number of Si-O and Si-N bonds in the entire film, respectively. For uniform films, the ratio, r, is equivalent to the ratio of Si-O and Si-N bonds around a *single* Si atom.

We have studied possible physical reasons for the nonlinear $\varepsilon$–x relation. One is the change in coordination number of constituent atoms depending on film composition, as proposed for Zr silicates in Ref.[5]. The other is the difference in the minimum atomic units that account for film composition and dielectric constant. The first reason is not the case in oxynitride films because the tie-line in the ternary composition diagram (Fig. 1) dictates constant coordination numbers. The nonlinear $\varepsilon$-x relation is therefore considered to originate from the second reason. In order to find out the minimum atomic unit that allows linear addition of polarizability, we assumed two models as depicted in Fig. 3. Minimum units around O and N are assumed in model (a), while those around Si are assumed in model (b). Using random bonding model [6] and Bruggeman's effective medium approximation [7], we calculated dielectric constant of oxynitride films as a function of film composition. The results (Fig. 4) indicate the superiority of model (b) to account for the experimental nonlinear $\varepsilon$–x relation. We conclude that the minimum unit for the polarizability of silicon oxynitride is a tetrahedron around Si.

Additionally, nitrogen depth profile has significant effect on direct tunneling current, owing to the nonlinear $\varepsilon$–x relation. The $\varepsilon$–x relation for a $SiO_2/Si_3N_4$ stacked film is almost linear to average film composition, in contrast to the nonlinear $\varepsilon$–x relation for uniform films. The difference in $\varepsilon$ is reflected in direct tunneling current. For equivalent nitrogen concentration, uniform nitrogen distribution is effective in reducing the tunneling current (Fig. 5).

## 4. Conclusions

We have experimentally established the $\varepsilon$–x relation for homogeneous, ultra-thin silicon oxynitride films. The nonlinearity in the $\varepsilon$–x relation indicates that a tetrahedron around Si is the minimum unit for polarizability. Due to the nonlinear $\varepsilon$–x relation, uniform nitrogen depth profile is effective in reducing direct tunneling current.

**References**

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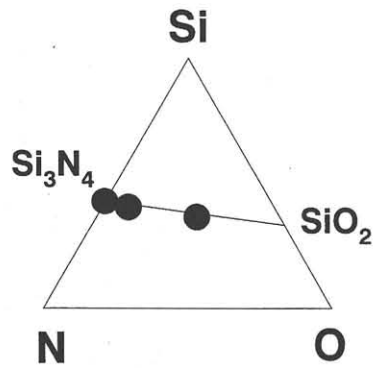


**Fig. 1** Composition of ultra-thin silicon oxynitride films deposited by PECVD. The presence of data on the tieline between $Si_3N_4$ and $SiO_2$ indicates constant coordination numbers of 2, 3 and 4 for O, N and Si, respectively.

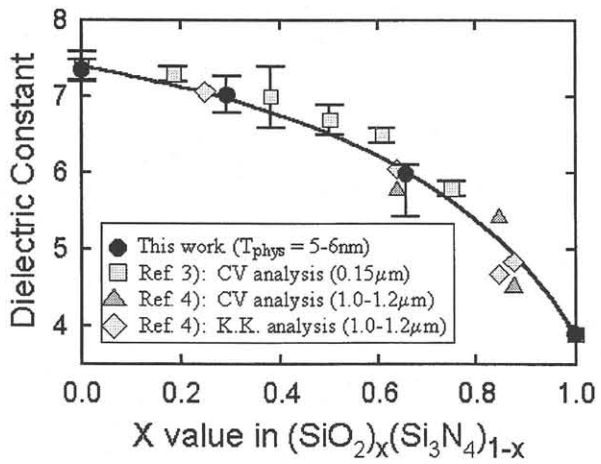


**Fig. 2** The relation between dielectric constant and film composition of silicon oxynitride films. Regardless of film thickness, dielectric constant is described with an empirical relation (solid curve) : $\varepsilon = \varepsilon(SiO_2)\, r + \varepsilon(Si_3N_4)\,(1-r)$ where $r = [Si\text{-}O] / ([Si\text{-}O] + [Si\text{-}N]) = x / (3 - 2x)$.

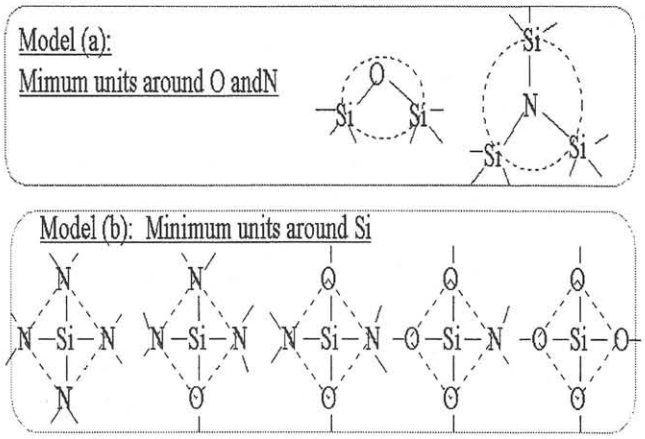


**Fig. 3** Two minimum unit models for dielectric constant of oxynitride films. The volume fraction ($f_i$ where $\Sigma f_i=1$) of each unit is calculated as a function of film composition, based on random bonding model [6]. The dielectric constant ($\varepsilon$) of oxynitride is calculated with Bruggeman's effective medium approximation [7]. The dielectric constant $\varepsilon$ is expressed as $\Sigma f_i(\varepsilon_i-\varepsilon)/(\varepsilon_i+2\varepsilon)=0$ where $\varepsilon_i$ is dielectric constant of each unit.

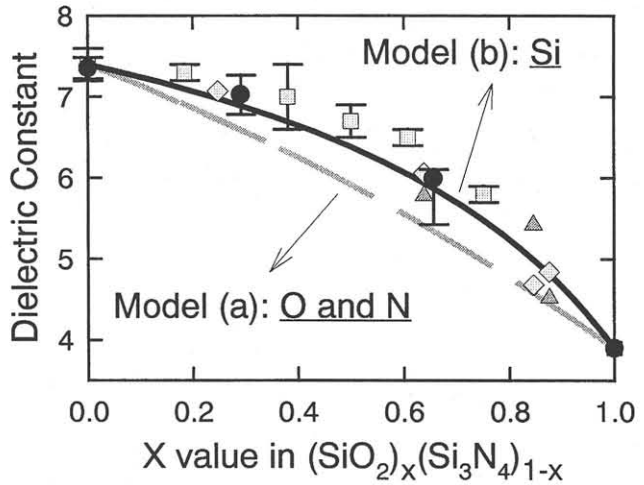


**Fig. 4** Results of model calculations. Model (b) (solid curve) accounts for the nonlinear $\varepsilon$-x relation better than model (a) (dashed curve).

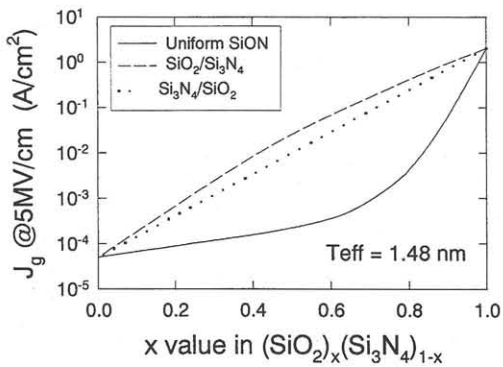


**Fig. 5** Calculated direct tunneling current (electrons) of ultra-thin uniform and stacked films. $SiO_2/Si_3N_4$ and $Si_3N_4/SiO_2$ indicate electron injection from $SiO_2$ and $Si_3N_4$, respectively.