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Net negative charge in low-temperature SiO_2 gate dielectric layers

A. Boogaard *, A.Y. Kovalgin, R.A.M. Wolters [1]

MESA+ Institute for Nanotechnology, Chair of Semiconductor Components, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands

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ABSTRACT

SiO_2 gate dielectric layers (4–60 nm) were grown (0.6 nm/min) by plasma-enhanced chemical vapor deposition (PECVD) in strongly diluted silane plasmas at low substrate temperatures. In contrast to the well-accepted positive charge for thermally grown silicon dioxide, the net oxide charge was negative and a function of layer thickness. Our experiments suggested that the negative charge was created due to unavoidable oxidation of the silicon surface by plasma species, and the CVD component added a positive space charge to the deposited oxide. The net charge was negative under process conditions where plasma oxidation played a major role. Such conditions include low deposition rates and the growth of relatively thin layers.

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1. Introduction

We have grown SiO_2 gate dielectric layers at 150 °C by remote plasma-CVD. The aim of this work was to enable the fabrication of electronic devices on top of a complete integrated circuit, which follows the contemporary ideas of 3-D integration [1]. To keep the circuit intact, the substrate temperature should remain low. We recently showed the applicability of our gate dielectrics to low-temperature TFTs by demonstrating competitive mobility values, good ring oscillator performance, and low off-currents [2]. These layers exhibited excellent I–V characteristics and low interface state densities (D_{it}) despite the low-temperature and plasma nature of the deposition. In contrast to thermally grown silicon dioxide, the net charge appeared to be negative and a function of layer thickness. The latter observation is the main topic of this paper. We studied this effect because of its novelty and the expected impact on the threshold voltage of field-effect devices and their performance. This fixed charge may be exploited in particular applications, e.g., the reduction of recombination losses in photovoltaic devices by electrostatically shielding the minority charge carriers using internal electric fields [3].

We demonstrate that two mechanisms can contribute to the film growth and the formation of charges, namely plasma oxidation of the silicon substrate and chemical vapor deposition. We suggest that plasma oxidation mainly results in the growth of the first nm-range of oxide thickness, thereby offering a possible mechanism for the negative charge formation.

2. Experimental

Silicon dioxide films were grown by means of remote inductively coupled plasma-enhanced chemical vapor deposition (IC-PECVD) in Ar–N_2O–SiH_4 plasmas at 150 °C and at a total pressure of 1 Pa as described previously [4]. The gas phase contained 0.08% SiH_4 and 18% N_2O. Depositions at higher total pressures or higher partial pressures of SiH_4 resulted in oxide layers with higher leakage currents and are not discussed here [4].

Films were deposited on H-terminated Si-wafers (n-type <1 0 0>) that received standard cleaning. The deposition process was monitored in situ using a J.A. Woollam M2000 spectroscopic ellipsometer (SE). MOS capacitors were implemented by sputtering 1-µm Al over the oxide, followed by lithography and etching processes to define 0.06, 0.1, and 0.2 mm^2 square capacitors. An Al layer was also sputtered on the backside of the Si wafer.

All wafers were subjected to post-metallization annealing (PMA) for 10 min at 400 °C in humid, ambient N_2 (N_2 bubbled through de-ionized water at room temperature). Some wafers received a post-oxidation anneal (POA) in N_2 at 900 °C for 30 min prior to the Al metallization. The high frequency (10 kHz–1 MHz) capacitance–voltage (C–V) and current density–voltage (J–V) measurements were carried out using a Hewlett–Packard 4275A multi-frequency meter and a Hewlett–Packard 4140B pA meter, respectively.

Expression (1) was used to calculate the influence of the oxide charge density in a volume ($\rho_{ox}(x)$) on the flatband voltage V_{FB}:

$$V_{FB} = \varphi_{ms} - \frac{1}{C_{ox}} \int_0^{T_{ox}} \frac{x}{T_{ox}} \rho_{ox}(x) \mathrm{d}x, \qquad (1)$$

where φ_{ms} is the metal–semiconductor work-function difference, x is the distance from the gate, T_{ox} is the thickness of the oxide, and

* Corresponding author. Tel.: +31 53 4892727, fax: +31534891034.
E-mail address: a.boogaard@utwente.nl (A. Boogaard).
[1] Also with NXP Research, HTC 4, 5656 AA Eindhoven, The Netherlands.

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C_{ox} is the oxide capacitance [5]. A determination of the charge distribution and its location in the oxide was needed to solve the integral. For thermally grown oxides, the flatband voltage was calculated using the standard expression $V_{FB} = \varphi_{ms} - Q_f/C_{ox}$ where Q_f is the fixed charge near the Si–SiO_2 interface [5].

Importantly, despite the deposition temperature of 150 °C, the deposited films are of high quality. They exhibit very low leakage currents at the electric field strength of 6.5 MV/cm, which is comparable to the leakage currents of thermally grown oxides (Fig. 1a). The ledges at 7–8 MV/cm are probably related to a conduction mechanism caused by bulk traps e.g. due to excess of Si [6]. The ledges in this work are much smaller compared to those measured earlier for films with a higher SiH_4 fraction of 0.8%. The latter were also observed at lower electric fields between 2 and 6 MV/cm [4]. A very low midgap-D_{it} of 3×10^{10} eV^{-1} cm^{-2} was obtained from the QS and HF measurements presented in Fig. 1b.

3. Results and discussion

In Fig. 2, in situ SE measurements are presented from the first few minutes of the deposition (open circles). The figure shows a fast initial oxide growth regime that gradually transfers into a linear regime with a growth rate of 0.6 nm/min. The figure also depicts oxide growth without SiH_4, i.e., plasma oxidation only (solid triangles). The inset of Fig. 2 shows the calculated growth rates of the oxidation and CVD components. One can conclude that initial oxide formation is due to oxidation of Si. Plasma oxidation dominates for the first 2.5 nm of oxide growth and is replaced by CVD for the thicker layers.

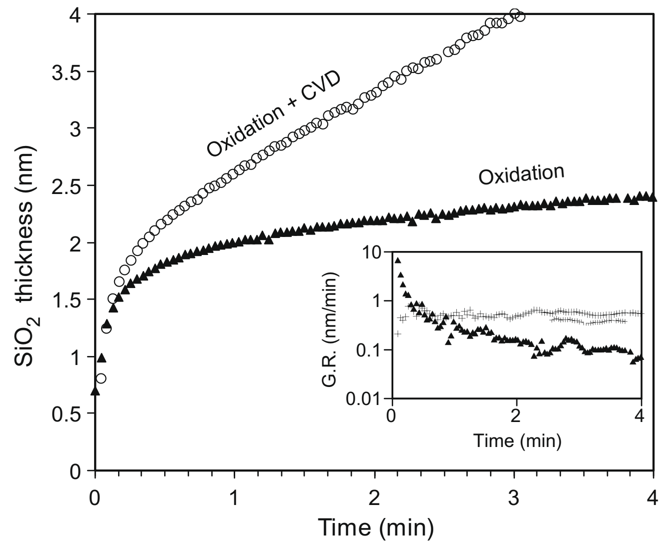

Fig. 2. In situ thickness measurements without (▲) and with (o) silane; other conditions were the same and are mentioned in the Section 2. In the inset, the growth rates are shown for the CVD (+) and the oxidation (▲) components.

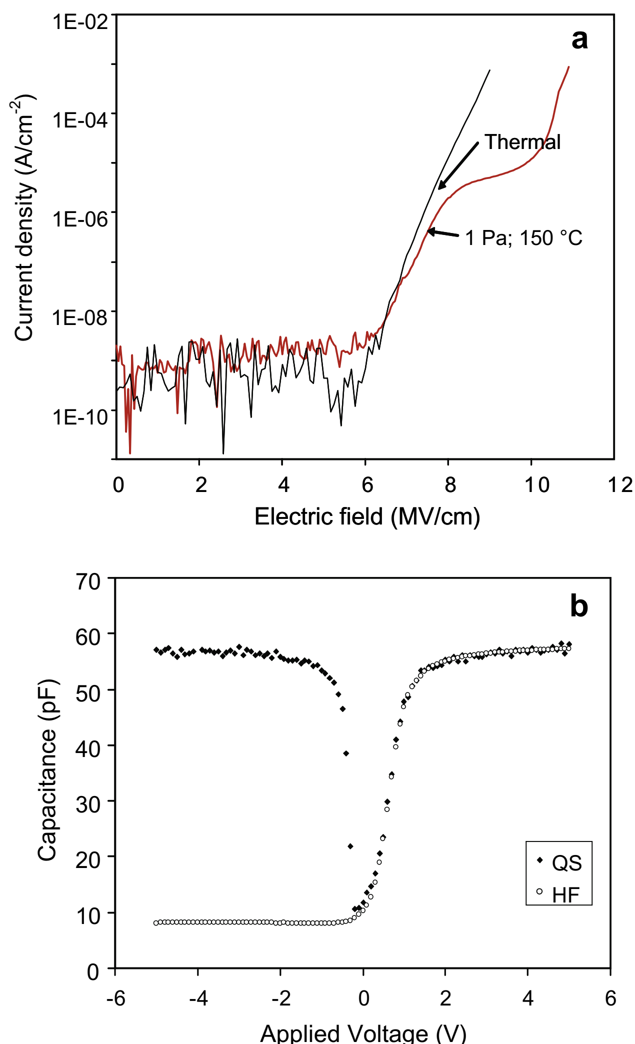

Fig. 1. (a) J–E characteristics of oxide layers from PECVD (35 nm) and from thermal growth at 950 °C (25 nm); the electric field (E) was calculated as (V–V_{FB}) divided by the thickness; (b) C–V curves of a 35-nm PECVD SiO_2 layer.

The presence of two formation mechanisms was expected to influence layer properties. This influence could be observed particularly for very thin layers when thicknesses of the two differently formed sub-layers were comparable. Instead of a positive charge, as normally is observed in SiO_2 films, a *negative* oxide charge, 5×10^{11} cm^{-2}, was calculated from the high-frequency C–V curve (see Fig. 1b).

We measured φ_{ms} on thermally grown oxide (dry oxidation at 950 °C followed by 20-min POA) because of the variation in published φ_{ms} values. As an example, for Al on n-type Si with a doping level of 1.5×10^{15} cm^{-3}, Sze [7] published a value of −0.2 V while Pierret [8] reported −0.3 V. Rewriting the expression of V_{FB} one gets $V_{FB} = \varphi_{ms} - Q_f\, T_{ox}/K_{ox}\varepsilon_0$ where Q_f is the fixed charge near the Si–SiO_2 interface, T_{ox} is the oxide thickness, K_{ox} is the oxide dielectric constant and ε_0 is the permittivity of vacuum.

Fig. 3a shows a plot of V_{FB} versus oxide thickness. The data set of thermally grown oxide has a slope of $-Q_f\, T_{ox}/K_{ox}\varepsilon_0$ and an intercept on the V_{FB} axis of $\varphi_{ms} = -0.214$ V (Q_f is assumed to be the same and near the Si interface for all data points) [9]. A *positive* charge of 8×10^{11} cm^{-2} was calculated for the thermally grown oxide (see crosses in Fig. 3b); the same charge density can be obtained from the slope of the dotted curve in Fig. 3a.

Analysis of the high-frequency C–V curves of our PECVD layers reveals a non-linear trend of the flatband voltage in relation to thickness (see open diamonds in Fig. 3a). If we compare the curves of thermal oxides and PECVD oxides in Fig. 3a, we observe different signs of the slopes, indicating positive and negative net-charges. If Q_{ox} is calculated for the given PECVD oxides using the expression $V_{FB} = \varphi_{ms} - Q_{ox}/C_{ox}$, one finds that thinner layers contain a higher amount of negative charge compared to thicker films (see open diamonds in Fig. 3b). We attribute this important and novel result to the initial plasma oxidation step, which cannot be avoided. Thus, the plasma oxide becomes dominant for thinner layers. The plasma-oxidized region near the Si-interface may be responsible for the negative charge formation.

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