Nitridation of Silicon-Dioxide Films Grown on 6H Silicon Carbide

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***Abstract*—This letter addresses the question of why it is possible to grow high-quality oxide films on N-type but not on P-type SiC. It provides results which indicate that the oxide/SiC interface would be inferior to the oxide/Si interface for both, N-type and P-type SiC, if it were not for the beneficial effects of nitrogen incorporation. The letter presents, for the first time, results on nitridation of thermally grown oxides in NO and N_2O. The results demonstrate that the oxides grown on P-type can be improved by NO annealing, but not by N_2O annealing.**

I. INTRODUCTION

SUCCESSFUL growth of silicon-dioxide films on silicon-carbide substrates may mark the beginning of a new era in semiconductor electronics. Metal-oxide-semiconductor (MOS) devices based on a wide band-gap material such as silicon carbide have the potential to revolutionize power electronics, microwave systems, high temperature, and many other applications.

At present, it is not understood why it is possible to grow high-quality oxide films on N-type but not on P-type SiC [1]–[6]. Initially, it was speculated that the aluminum (used as the P-type dopant in SiC) was causing this problem [2]–[4]. Later, it has been shown that boron-doped P-type SiC does not improve the quality of the oxide [5], and that aluminum is also present in high-quality oxides grown on N-type SiC [6].

In this letter, we present results which shift the focus from the potential problems with the P-type SiC to the beneficial role of nitrogen, used as a dopant in the N-type SiC. We report, for the first time, results on nitridation of O_2-grown oxides in NO and N_2O. The results suggest that the oxides grown on P-type SiC can be improved by NO annealing, which is a significant step toward a successful fabrication of enhancement type N-channel MOSFET's on SiC.

II. EXPERIMENTAL DETAILS

Si-faced 6H SiC wafers, manufactured by CREE Research, were used in this experiment. The concentration of the nitrogen doped N-type wafer was 4.8×10^{17} cm^{-3}, while the concentration of the aluminum doped P-type wafer was 2.5×10^{18} cm^{-3}. The wafers were cut into approximately 1.5×1.5 cm pieces, and cleaned by both an H_2SO_4:H_2O_2 solution and RCA cleaning process. Immediately before the oxidation, the samples were dipped in 1% HF for 60 s. The SiC carbide pieces were placed onto a 6-in silicon wafer, to perform the oxidation in an AG610 rapid-thermal processing (RTP) unit. The oxidation was performed in six 5-min. steps (to allow cooling of the RTP unit) in high-purity O_2 at around 1100 °C. After the oxidation, two sets of samples received an additional 5-min treatment at the same temperature: one set of samples was exposed to a 99% (chemical pure grade) NO, while the other was exposed to a high-purity N_2O environment. Following the oxidation and the nitridation of the samples, aluminum was evaporated at the top and the back of the samples, and circular 300-μm dots defined at the top by a photolithography process to create MOS capacitors. No post-metal annealing is performed, to avoid masking the defects created during the oxidation and/or nitridation. MOS capacitor characterization was performed by high-frequency (100 kHz capacitance–voltage (C–V) and conductance–voltage measurements, using a computer-controlled HP4284A LCR meter.

III. Si BACKGROUND, SiC RESULTS, AND DISCUSSION

The increasing demand for thinner and better gate dielectrics in silicon technology motivates extensive investigations into potential benefits of nitridation of oxide films grown on Si. Annealing in NO and N_2O appear to be the two most promising techniques. While both techniques lead to incorporation of nitrogen at the interface, the annealing in N_2O leads to new oxide growth [7], as opposed to the annealing in NO which nitrides the interface with virtually no new oxide growth [8]–[11]. The nitrogen accumulation at the interface is related to observed improvements of the electrical characteristics of oxide/silicon interface [8]–[14]. Similar effects have been observed when the oxide is grown on nitrogen implanted polysilicon [15].

It is indicative to correlate these silicon-related results to the results of Palmour *et al.* [16], showing a similar accumulation of nitrogen at the oxide/silicon-carbide interface during thermal oxidation of nitrogen-doped N-type SiC substrate. This leads us to a hypothesis that the nitrogen incorporation improves the oxide/N-type silicon-carbide interface, which would otherwise remain inferior compared to the oxide/silicon interface. Furthermore, this suggests that the quality of oxides grown on P-type SiC could be improved by an appropriate nitridation process.

De Meo *et al.* [17] showed that oxides on SiC substrate can directly be grown in N_2O rather than O_2 or H_2O. However, they could not demonstrate an improvement in the interface characteristics of N_2O grown oxides on N-type SiC. Having observed a number of differences in the effects of NO and N_2O

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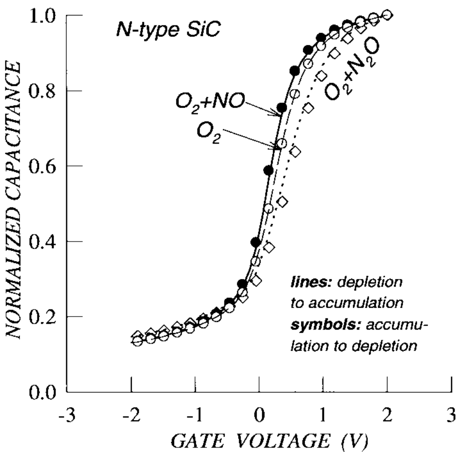

Fig. 1. High-frequency (100 kHz) C–V measurements of MOS capacitors created on N-type 6H SiC.

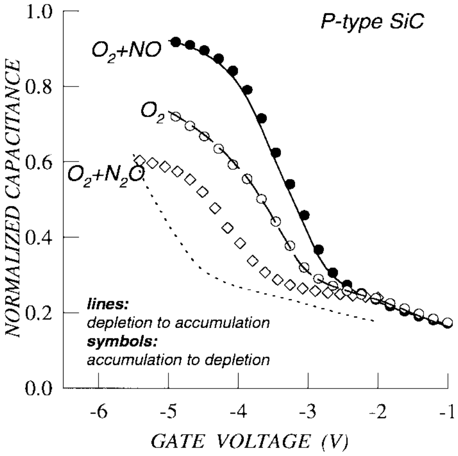

Fig. 2. High-frequency (100 kHz) C–V measurements of MOS capacitors created on P-type 6H SiC.

TABLE I

EFFECTS OF NO AND N_2O ANNEALING ON THE OXIDE CHARGE AND INTERFACE TRAP DENSITY OF MOS CAPACITORS CREATED ON 6H SiC

	O_2	O_2+NO	O_2+N_2O
	N-type ($\phi_{ms}=0.15V$)		
t_{ox} $[nm]$	3.5	3.5	3.9
C_{FB}/C_{ox}	0.62	0.62	0.65
V_{FB} $[V]$	0.3	0.2	0.5
Q_{ox} ($@V_{FB}$) $\times 10^{12} cm^{-2}$	−0.9	−0.3	−1.9
D_{it-max} $\times 10^{11}$ $cm^{-2}eV^{-1}$	1.1	0.3	1.3
	P-type ($\phi_{ms}=-2.70V$)		
t_{ox} $[nm]$	3.5	3.5	3.9
C_{FB}/C_{ox}	0.79	0.79	0.81
V_{FB} $[V]$	< -5.0	−3.9	< -5.5
Q_{ox} ($@V_{FB}$) $\times 10^{12} cm^{-2}$	> 14	7.3	> 15

on oxides grown on Si [9], [18], [19], we decided to anneal oxides grown on SiC in both NO and N_2O atmosphere. We also included the both N-type and P-type SiC substrates. The main results are presented in Figs. 1 and 2, and Table I.

The oxide thicknesses, shown in Table I, were calculated from the accumulation capacitances of the N-type samples, and assumed to be the same for the corresponding P-type samples. Direct calculations of the oxide thicknesses on P-type samples would not be meaningful as the C–V curves of P-type samples do not saturate at negative voltages. The HF C–V curves are normalized accordingly, and shown for the both sweeping directions. To calculate the work-function differences ($\phi_{\rm ms}$) shown in Table I, the following parameters are used: the work-function of aluminum $\phi_m = 4.1$ eV [20], the silicon-carbide electron affinity $q\chi = 3.85$ eV [21], and the intrinsic carrier concentration of 6H SiC $n_i = 1.6 \times 10^{-6}$ cm^{-3} [22]. The flat-band voltages were determined from the flat-band capacitances, calculated by the standard expression [23]. The oxide-charge densities were calculated as $Q_{\rm ox} = -C_{\rm ox}(V_{FB} - \phi_{\rm ms})/q$. The interface-trap densities $D_{\rm it}$ were determined using the conductance technique [24].

Analyzing the presented results, the following two observations are made: 1) the effects of annealing in either NO or N_2O are much more pronounced in aluminum-doped (P-type) SiC samples, compared to nitrogen-doped (N-type) SiC samples, 2) NO annealing improves, while N_2O annealing deteriorates the electrical characteristics of thermally grown oxides on either P- or N-type SiC substrate.

The first point directly supports the hypothesis on the beneficial role of nitrogen, as the stability of the oxides grown on the nitrogen-doped SiC substrates can be explained by the nitrogen present at the interface before any nitridation treatment was applied. As opposed to the relative stability of N-type samples, the electrical characteristics of the oxides grown on P-type substrates were significantly improved by the NO annealing. The C–V curve of the NO-annealed sampled almost reaches the accumulation value observed on the N-type samples. It is much closer to the ideal C–V curve than the C–V curve of O_2 (not-nitrided) sample, which shows the problems observed by other researchers [1]–[6]. It appears the presence of a significant amount of interface traps causes such a stretch that the C–V curve cannot reach the accumulation capacitance up to −5 V, which is the breakdown voltage.

The results clearly demonstrate a deterioration of the interface characteristics during the N_2O annealing. Again, this is especially pronounced for the P-type samples. Different C–V curves appear for the different sweep directions during the measurements, indicating that the equilibrium cannot be achieved due to the action of slow traps. In addition, a negative voltage shift is obvious, indicating the presence of a significant amount of positive charge in the oxide or at the interface with SiC. We believe it would be very interesting to study these effects of N_2O annealing, as it may help to understand better the nitridation of thermally grown oxides not only on SiC, but also on Si substrates.

IV. CONCLUSIONS

In conclusion, we presented results on NO and N_2O annealing of oxides grown on N-type and P-type 6H-SiC substrates. The results show that the annealing significantly affected the P-type oxides, while the effects in N-type oxides were marginal. This indicates that a stable nitrided interface is created during the oxidation in the case of nitrogen-doped N-type SiC substrates. It is also demonstrated that the oxides grown on P-type can be improved by NO annealing, but not by N_2O annealing.

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