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Abstract. A chloride-based chemical-vapor-deposition (CVD) process has been successfully used to grow very high quality 3C-SiC epitaxial layers on on-axis α-SiC substrates. An accurate process parameters study was performed testing the effect of temperature, *in situ* surface preparation, precursor ratios, nitrogen addition, and substrate polytype and polarity. The 3C layers deposited showed to be largely single-domain material of very high purity and of excellent electrical characteristics. A growth rate of up to 10 μm/h and a low background doping enable deposition of epitaxial layers suitable for MOSFET devices.

Introduction

The cubic polytype of SiC has been one of the most studied because it can be easily grown on silicon substrates, but also for its higher electron drift velocity and electron mobility [1]. In addition it has been suggested as a suitable polytype for MOSFET devices thanks to the lower defect density in the SiC/SiO$_2$ interface as compared to 4H-SiC [2], reaching blocking voltages up to 1500 V and current handling up to 100 A. 3C-SiC is also proposed as a substrate in the zinc blende structure for heteroepitaxial growth of other semiconductor materials, such as GaN [3].

3C-SiC is thermodynamically not stable [4], therefore it is usually grown by heteroepitaxial process, either on silicon [5] or α-SiC substrates [6]. The quality of 3C grown on silicon is not very high because of the high density of defects, generated by the large lattice and thermal expansion coefficient mismatchs between the materials. Higher quality 3C can be grown on the common hexagonal (4H and 6H) substrates, which has been verified by CVD [5, 6] and VLS [7]. In this study we have used chloride-based CVD to grow 3C on 4H- or 6H-SiC (0001) substrates. The presence of chlorine has shown to affect the formation of 3C-SiC on these surfaces while simultaneously granting a wider window of operating parameters, especially at the low temperatures required that favor the 3C formation [8].

Experimental procedure

The epitaxial growths were performed in a horizontal hot-wall reactor with a RF-heated tapered susceptor [9]. The precursors were silane (SiH$_4$), ethylene (C$_2$H$_4$), and hydrogen chloride (HCl), in a hydrogen carrier (H$_2$). The process was performed at a pressure of 200 mbar.

Several growth parameters were explored. 2 x 2 cm^2 samples were used as substrates, cut from different on-axis wafers: Si-face 4H-SiC; Si-face 6H-SiC; and occasionally C-face 4H-SiC. Different *in situ* etching conditions were applied by adding C$_2$H$_4$, SiH$_4$, or HCl to the carrier gas. Temperatures from 1300 to 1500 °C were tested, and different C/Si (0.4 to 1.6) and Cl/Si ratios (0 to 30) were used. Most samples were undoped, but nitrogen additions were tested at different flows (0.5 to 200 sccm).

The quality of the material and the polytype was assessed by: optical microscopy with Nomarski interference optics (NDIC); low temperature photoluminescence (LTPL) using the 244 nm Ar laser

line; and electron beam scattering diffraction (EBSD) in a SEM. Atomic force microscopy (AFM) was used to analyze the surface roughness of the smoothest 3C epilayers obtained. The thickness of the samples could be measured by FTIR reflectance measurements.

For the electrical characterization the samples were chemically cleaned and the natural oxide was removed using HF. The Ni contacts were directly evaporated on the surface but in the case of Au deposition an additional surface treatment was added consisting of a thermal oxidation for 2 hours under UV irradiation at 200 °C to saturate the surface states. I-V and C-V measurements were performed at room temperature. Deep-level-transient-spectroscopy (DLTS) investigations were done between 100 and 450 K. The reverse bias was $V_r = -2$ V, and in the case of 4H-SiC substrate $V_r = -5$ V. During the 10 ms pulse period, the voltage was reduced to $V_r = -0.5$ V. The transients were evaluated using a lock-in simulator.

All growth experiments were done using the same sequence of steps: Cleaned samples were loaded into the reaction chamber and evacuated by a turbo pump to a vacuum in the 10^{-4} mbar range; The system was heated to an intermediate temperature of 1200 °C while the carrier gas and pressure were set; The subsequent temperature ramp-up to the deposition temperature was done while adding an etching agent; Growth was performed for 60 minutes; The system was cooled down in hydrogen atmosphere. Every tested process parameter had a very important effect on the grown polytype and on the quality of the material.

Results and discussion

Temperature was the most effective parameter, affecting mainly the 3C morphology but also determining the polytype depending on the temperature ramp-up conditions. At temperatures below 1400 °C 3C-SiC was always obtained, while at temperatures between 1400 °C and 1600 °C the polytype was determined by the ambient in the reaction chamber during the temperature ramp-up.

In situ **etching.** The etchant gas, if any, was added during the temperature ramp-up from 1200°C to the deposition temperature. If C_2H_4 was added to the carrier gas, the epitaxial layer polytype would be 3C; otherwise (flowing SiH_4 or pure H_2) the substrate polytype was replicated totally or partially. HCl addition led to 3C layers with several disordered domains.

C/Si ratio. The carbon input was very important on the morphology of the 3C layers, but its effect was always tightly connected with the deposition temperature. At temperatures above 1400 °C the epilayers were always characterized by the presence of double position boundaries (DPBs) regardless of the C/Si ratio. At temperatures between 1300 °C and 1400 °C an excess of silicon species helped to achieve almost single domain 3C-SiC by using C/Si ratios below 1.

Cl/Si ratio. At temperatures between 1300 °C and 1400 °C the Cl/Si ratio had to be kept above 3 to avoid the formation of silicon droplets on the surface, but for ratios higher than 9 ordered DPBs appeared on the surface. For higher Cl/Si ratios the epilayer turned into a polycrystalline layer

Nitrogen addition. It has been reported that nitrogen could have a stabilizing effect on the 3C polytype [10], therefore different amounts of nitrogen were added. Small amounts (below 1 ml/min) were actually beneficial in making only one 3C domain prevailing over the other, resulting in largely single domain 3C-SiC epilayers. Flows above 10 ml/min were detrimental to the epitaxial layer, since a lot of silicon aggregates were formed, indicating that nitrogen atoms compete with carbon atoms when incorporating in the SiC lattice.

Substrate. 4H and 6H on-axis Si-face substrates did not exhibit a marked effect on the heteroepitaxial growth of 3C-SiC, irrespective of the different growth parameters. A few experiments were performed on C-face 4H samples with the optimum growth conditions, including the *in situ* C_2H_4 etching, but the epilayers always turned out to be 3C-SiC polycrystalline layers. We speculate that in this case the C-face surface, being already carbon terminated, did not benefit from the C_2H_4 *in situ* treatment.

Characterization. Most of the epilayers grown had a thickness of 10 to 15 μm as measured by FTIR reflectance resulting in a growth rate of 10-15 μm/h. Optical microscopy was used to analyze the epilayers' morphology, as described in the previous section. AFM was used to corroborate the
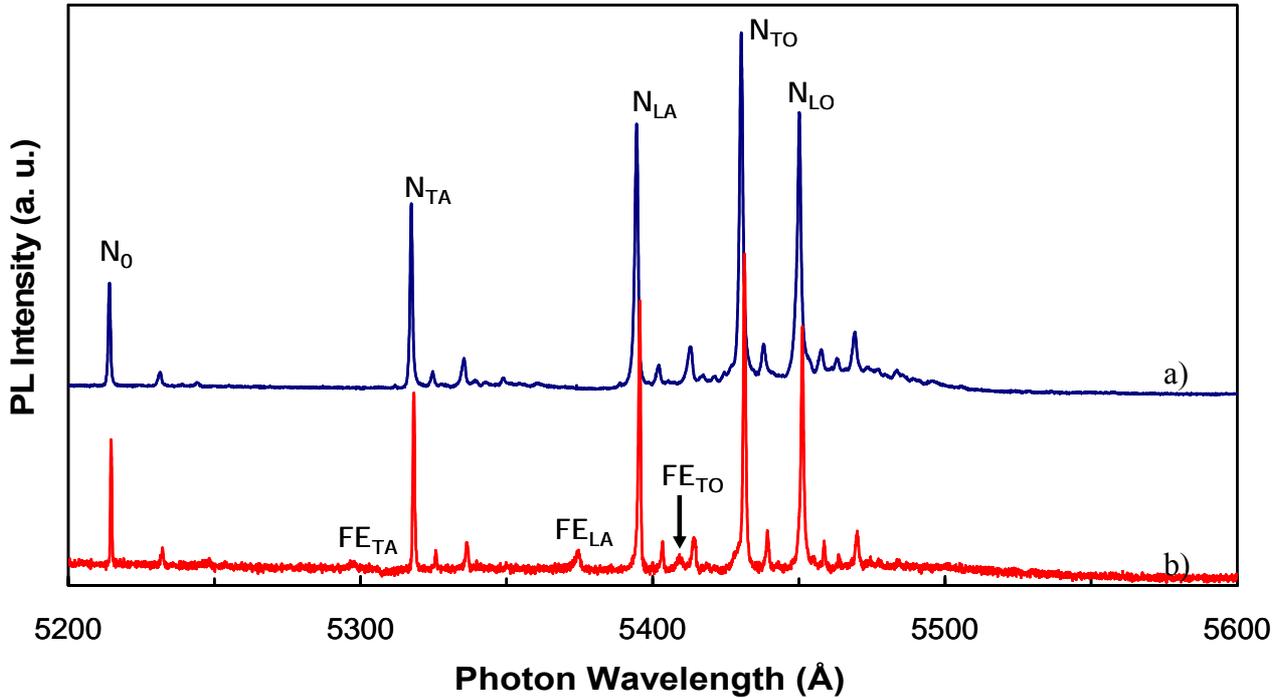
Fig. 1: LTPL spectra of the near band gap emission of 3C layers grown at 1365 °C, in-situ preparation with C_2H_4 (10 sccm), Cl/Si = 6, and a C/Si ratio of: a) 0.75; b) 1. The non-labeled lines are the multi-bound excitons lines

high quality of the best samples displaying a very low roughness (4 Å on a 10x10 μm^2 area) and a step structure. LTPL was performed at 2K and confirmed the high quality of the epilayers since the 3C near band gap luminescence was dominant and revealed very sharp and narrow multi-exciton lines and even free-exciton (FE) lines (Fig. 1).

EBSD was used to analyze the polytype of the epilayers and in case of 3C-SiC the presence of domains with two possible orientations (60° rotated). It was possible to clearly see the different morphologies and the presence of double position boundaries in several samples (Fig. 2a,c). It also confirmed that the layers grown with a small nitrogen flow addition were largely single domain 3C, and only a few defective areas showed the different orientation (Fig. 2b,d).
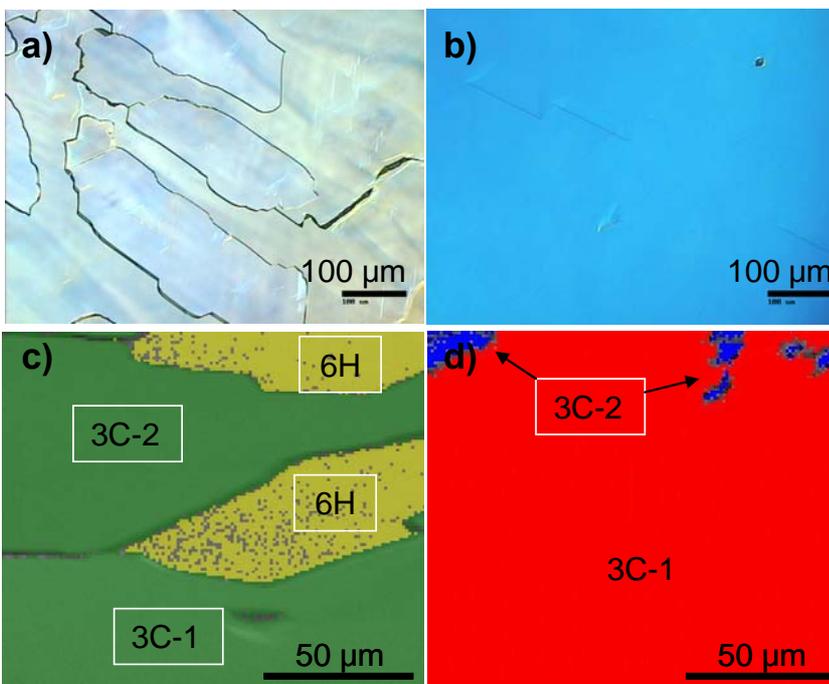
Hg probe C-V measurements showed a background doping concentration (N_d-N_a) in the low $10^{15} cm^{-3}$. The reverse leakage at $V_r = -2$ V was less than 1.5×10^{-8} A. Three different samples were selected for DLTS measurements, the net donor concentrations of these samples were determined using C-V: 1.2×10^{16} cm^{-3} for the 3C-SiC on

Fig. 2: NDIC (a, b) and EBSD images (c, d) of 3C layers grown with in-situ preparation with $C_2H_4 = 10$ sccm, Cl/Si = 6, C/Si ratio = 0.75, and different temperatures: a,c) T=1500°C; b,d) T=1365 °C and $N_2 = 0.05$ ml/min.

6H-SiC, 4.5×10^{15} cm^{-3} for the 3C-SiC on 4H-SiC and 1.4×10^{16} cm^{-3} for a 3C-SiC epilayer grown on a silicon substrate. The DLTS measurements (Fig. 3) resulted in one dominant peak at about 250 K ($E_a = 0.60$ eV) in all three samples. This peak is similar to the W6 peak reported by Weidner et al. [11]. The DLTS spectrum of the 3C-SiC grown on Si shows additional peaks at about 150 K and 450 K, which were reported on earlier.
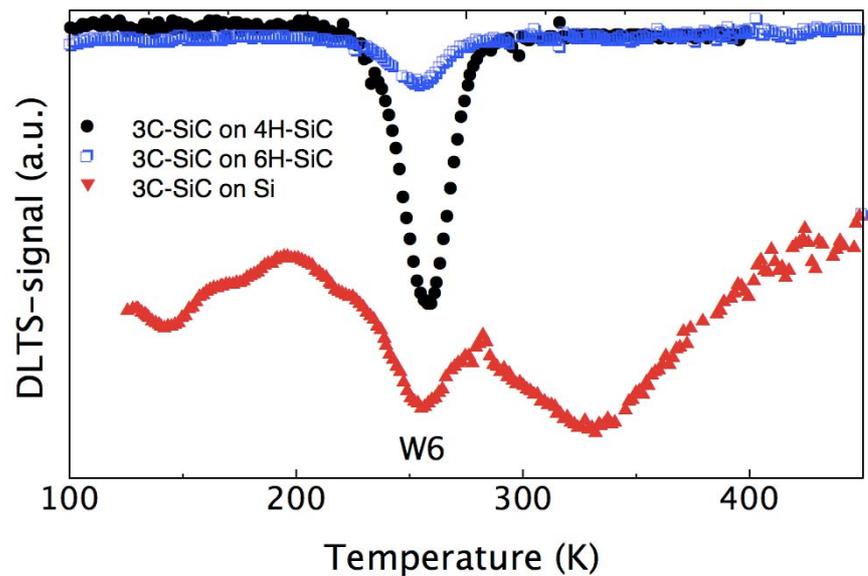

Fig. 3: DLTS spectra of as-grown 3C-SiC grown on different substrates 4H-, 6H-SiC and Si. DLTS parameters: rate window $(4.7 \text{ s})^{-1}$, $t_p = 10$ ms, $V_p = 1.5$ V and $V_r = -2$ V, in case of 4H-SiC: $V_p = 4.5$ V and $V_r = -5$ V.

Conclusions

In this study we demonstrated the growth of 3C-SiC on 4H- and 6H-SiC (0001) substrates by using chloride-based CVD. Very high quality and largely single domain 3C-SiC epilayers were grown at a temperature of 1365 ˚C, and a growth rate of 15 μm/h that was achieved thanks to the presence of chlorine in the gas mixture. IV and CV measurement confirmed the high quality of the 3C-SiC epitaxial layers. DLTS measurements revealed less defects than for layers grown on Si substrates. For 1500 ˚C growth temperature the electrical properties were better (lower leakage current), but the layer morphology was deteriorated by DPBs.

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