Concentration of N and P in SiC Investigated by Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

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Abstract. The concentration of nitrogen and phosphorous in SiC bulk material and epitaxial layers was investigated using time-of-flight secondary ion mass spectrometry (TOF-SIMS). The advantage of TOF-SIMS of acquiring a complete mass spectrum in a single run was used to identify the most sensitive atomic ion or ionic cluster for the selected element to be monitored. For the investigation of N with its intrinsic low ionization yield the use of a Cs containing cluster ion is necessary. Selection of a CNC₅⁺ cluster allows to reach a detection limit of about c₉₅,min ≈ 5·10¹⁶ cm⁻³. In the case of P the elemental ion was used. However, the adjacent mass of ³⁰SiH influences the P peak as well as its background and has to be suppressed. This can be achieved by limiting the residual gas re-adsorption during the measurement resulting in a detection limit of about c₉₅,min ≈ 5·10¹⁵ cm⁻³. These measurement parameters were used to investigate a single crystal SiC bulk sample grown by the modified Lely method with intentional P doping and an N doped epitaxial SiC layer sample.

Introduction

Dopant concentration levels and their spatial and depth distribution are of major importance for the electrical performance of semiconductor devices. Due to its high detection sensitivity secondary ion mass spectrometry (SIMS) is an established method for the determination of concentration levels of dopant materials and for diffusion studies during annealing [1]. Commonly, energy selective mass detectors are used such as magnetic sector analyzers, which provide very low detection limits. However, these methods restrict a depth profiling analysis to a pre-determined selection of ion masses. A specifically versatile SIMS method relies on the time-of-flight (TOF) detection technique. Here, the complete mass spectrum can be measured at every sample position without the above restriction of pre-selected masses. This allows for the detection of unexpected elements during the acquisition of a depth profile or chemical imaging. This versatility, however, is at the expense of sensitivity and puts the TOF-SIMS at a disadvantage compared to energy dispersive detectors in some cases. This can be, at least partly, compensated by using particularly selected measurement parameters for the different elements when ultra-low detection limits are required. In the present paper we demonstrate how by using Cs-cluster masses or well-tuned scanning conditions, the detection limits for N and P can be brought down to levels common for other SIMS machines.

Experimental

The experiments were performed using a commercial TOF-SIMS IV [2]. The secondary ions were generated by short pulses of a 25 keV Ga ion beam. Removal of material for depth profiling was carried out using a second ion beam from a Cs source. The Cs energies can be varied between 200
Both beams are chopped with a period varied between 20 µs and 100 µs and scanned over a variable acquisition area to allow for chemical imaging and depth profiling. Secondary ions are accelerated into the drift tube by a 2 kV potential providing the initial velocity distribution for the mass separation by time-of-flight analysis. With the drift time converted into atomic mass units (amu) a mass resolution of 9000 (m/Δm) at 29 amu can be achieved. Individual mass peak intensities (e.g. for CN, P, etc.) were integrated within a certain peak range and normalized using two unsaturated (for the purpose of avoiding dead counts by over-amplification) substrate related peaks in the adjacent mass range (e.g. C_{13}^{2} and SiC_{30}^{2} for P or C_{2}^{2} and SiC_{3}^{2} for CNC_{2}). The N and P concentrations were calibrated using ion implanted reference samples with a concentration maximum at 150 nm depth of 1.3·10^{20} cm^{-3} for N and 1.1·10^{20} cm^{-3} for P as determined by numerical simulations. The reference concentrations were implanted in commercial wafers. P dopant levels were investigated in bulk single crystals grown by the modified Lely method [3]. In addition, an N doped epitaxial layer sample grown by chemical vapor deposition was used [4].

**High sensitivity N detection by Cs-cluster ions**

Since the secondary ion yield for elemental N is comparatively low, for a high sensitivity N analysis, cluster ions have to be monitored. Here, the multi-mass detection by the TOF-SIMS technique provides a significant advantage, since in one experiment the most sensitive and least background affected cluster ion can be identified. However, cluster combinations with Si or C do not yield sufficient sensitivity for a low detection limit. Only the use of a Cs containing cluster provides high enough intensities combined with a low background. Yet, when measuring depth profiles through the ion implanted reference sample for a series of masses compatible to different Cs-clusters, it turns out that only the intensity of CNC_{2} at 291.811 amu shows any relation to the N

eV and 2 keV. Both beams are chopped with a period varied between 20 µs and 100 µs and scanned over a variable acquisition area to allow for chemical imaging and depth profiling. Secondary ions are accelerated into the drift tube by a 2 kV potential providing the initial velocity distribution for the mass separation by time-of-flight analysis. With the drift time converted into atomic mass units (amu) a mass resolution of 9000 (m/Δm) at 29 amu can be achieved. Individual mass peak intensities (e.g. for CN, P, etc.) were integrated within a certain peak range and normalized using two unsaturated (for the purpose of avoiding dead counts by over-amplification) substrate related peaks in the adjacent mass range (e.g. C_{2}^{13}C and SiC_{30}^{3} for P or C_{2}^{2} and SiC_{3}^{2} for CNC_{2}). The N and P concentrations were calibrated using ion implanted reference samples with a concentration maximum at 150 nm depth of 1.3·10^{20} cm^{-3} for N and 1.1·10^{20} cm^{-3} for P as determined by numerical simulations. The reference concentrations were implanted in commercial wafers. P dopant levels were investigated in bulk single crystals grown by the modified Lely method [3]. In addition, an N doped epitaxial layer sample grown by chemical vapor deposition was used [4].

**Figure 1:** Simulated N concentration in the ion implanted reference sample (left and lower axis) and corresponding experimental depth profile of the CNC_{2} (291.811 amu) peak (right and upper axis, sputter time given).

**Figure 2:** Mass spectrum in the range of the CNC_{2} peak for an epitaxial SiC layer with low N doping (raw data). The dashed vertical line indicates the nominal peak position at 291.811 amu.
Low level P concentration and residual H adsorption

Unlike for the case of nitrogen, phosphorous has a reasonably high secondary ion yield and can be analyzed using the elemental ion. Its sensitivity level and intensity dynamics exceed those of cluster ions as shown in fig. 3 for P and the two most sensitive clusters CP and C$_2$P. In the latter cases, the restriction arises from relatively high background contributions by $^{13}$C$^{30}$Si and $^{13}$C$^{1}$C$^{30}$Si, respectively. Yet, also the P peak at 30.974 amu is influenced by a second contribution, namely $^{30}$SiH, which is located at 30.981 amu. Certainly, the two peaks can be separated by our instrument (the corresponding mass resolution necessary would be 4500). However, for quantification a peak shape analysis would be required, which makes a suppression of the $^{30}$SiH peak desirable. Indeed, that can be achieved by fine-tuning the measurement parameters including a physical blocking of the preceeding masses. Nevertheless, the critical step is a reduction of the Ga scan area to prevent re-adsorption of hydrogen from the residual gas. The effect of these measures is shown in fig. 4 for an isolated $^{30}$SiH peak as found in the epitaxial layer sample in curves a (not suppressed) and b (suppressed). For a P concentration of about $4\cdot10^{17}$ cm$^{-3}$ normal measurement conditions yield a double peak (fig. 4c). With residual H suppression (the same parameters as for curve b) a small $^{30}$SiH contribution remains (curve d) which apparently results from H in the sample itself. P of $2\cdot10^{16}$ cm$^{-3}$ concentration appears only as a small shoulder at the low mass slope of the $^{30}$SiH peak under normal conditions (curve e). With H suppression the two peaks, P and $^{30}$SiH, respectively, can be clearly resolved (curve f). The detection limit achieved under optimized conditions can be estimated to about $c_{\text{P, min}} \approx 5\cdot10^{15}$ cm$^{-3}$.
Using these conditions \( c_p \) was measured for bulk grown SiC (by the modified Lely method) with intentional P doping on a dual-seed sample with simultaneous growth on the Si- and the C face [3,5]. The concentration varies for the two growth directions between \( 4 \cdot 10^{16} \text{ cm}^{-3} \) for the Si-face and \( 1 \cdot 10^{17} \text{ cm}^{-3} \) for the C-face, as measured in the middle of the boule. Close to the seed crystal the concentration is considerably lower (i.e. \( \approx 2 \cdot 10^{16} \text{ cm}^{-3} \)), but also in the surface region the concentration is reduced to about 50%. The corresponding N concentration levels obtained in the boule are \( 1.2 \cdot 10^{18} \text{ cm}^{-3} \) for the Si-face and \( 5.2 \cdot 10^{18} \text{ cm}^{-3} \) for the C-face.

**Summary and outlook**

The concentration of nitrogen and phosphorous in SiC samples was measured using the versatile TOF-SIMS technique. For the investigation of N, selection of a CNCs\(_2^+\) cluster allows a detection limit of about \( c_{N,\text{min}} \approx 5 \cdot 10^{16} \text{ cm}^{-3} \). In the case of P the residual gas re-adsorption during the measurement has to be limited which yields a detection limit of about \( c_{P,\text{min}} \approx 5 \cdot 10^{15} \text{ cm}^{-3} \). A further reduction of these values might be achievable by applying a curve fitting procedure or a peak line shape analysis. Other typical elements interesting in SiC technology, such as Al, B, O or others can also and simultaneously be analyzed without restrictions. Thus, the high spatial resolution of the TOF-SIMS technique may be used for detailed depth profiling and chemical imaging of low concentration dopants and – in combination – for a 3D analysis of concentration and contamination levels.

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**References**


