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A comparative study for profiling ultrathin boron layers in Si

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The carrier concentration-depth profiles of ultrathin boron layers in Si, grown by molecular beam epitaxy, are determined by the electrochemical capacitance-voltage (ECV) and the spreading resistance (SR) profiling techniques. Secondary ion mass spectrometry (SIMS) is employed as a base for the comparison of the results. It has been shown that, under carefully chosen conditions, both ECV and SR techniques are able to resolve ultrathin layers including a delta layer, however ECV match better with the results of SIMS than that of SR.

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1 Introduction

The routine growth of ultrathin layers such as delta doping spikes and their applications on devices has become possible with the advent of low-temperature epitaxial growth techniques such as molecular beam epitaxy (MBE) [1]. Characterisation of such ultrathin layers and understanding the properties of such profiles have been, in fact, a challenging analytical task of the resolution of the various techniques, each of which has its own capabilities and limitations. Indeed, a *multi*-technique approach is often necessary to fully characterise the structure. For example, transmission electron microscopy (TEM) images may provide useful information about lateral dopant distribution in a structure, but the relationship between intensity and concentration cannot be quantified. X-ray diffraction is a fast, non-destructive and high resolution method to assess the spatial localisation of dopants, but it is necessary to consider and model the strain induced by the dopant [2]. In principle some information about the dopant distribution function may be extracted from the position and relative intensity [3] however, as with TEM, sensitivity is poor. Cross-sectional field emission-scanning electron microscope (FE-SEM) images of boron-doped Si heterostructures are shown to be useful to map electrically active dopant profiles in two dimensions, nevertheless quantification needs to be improved [4]. With respect to direct dopant profiling, SIMS provides the most reliable assessment, but only of the chemical concentration [5]. In order to use the Hall technique, assumptions have to be made about the Hall factor, typically 0.75 for holes [6] and, uniformly doped or simple structures are needed. Conventional C-V technique is successfully employed to obtain a carrier concentration profile in a semiconductor structure or a device. However the major drawback of the technique is the limitation to the accessible depth that is set by electrical breakdown at high bias, which restricts the profiling of delta layers with a sheet density of less than $1x10^{13}$ cm^{-2} (for example see [1]). The present work demonstrates the capabilities of the ECV and SR techniques for profiling ultrathin boron layers in Si by comparing their results with the help of SIMS data.

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2 Experimental

The boron-doped sample employed for this study was grown on p^{++} Si (100) substrate at 480°C to minimise diffusion during growth and, ensure full activation and minimal surface segregation [7, 8]. A modified VG Semicon V90S MBE system was employed, using electron beam evaporated Si source and an elemental B effusion cell [9]. The Si substrate was annealed *in-situ* at 850 °C to remove SiO_2 and then a Si buffer was deposited as the temperature was cooled down to the growth temperature. The structure (#33/9) contains boron spikes doped nominally at $2x10^{19}$ cm^{-3}. The layer thicknesses were varied from 64 nm to 2 nm and then a delta layer was deposited with a sheet density of $3x10^{13}$ cm^{-2}. The spikes were separated by 100 nm thick Si layers with an intentional (*p*-type) background doping level of $2\text{-}3x10^{16}$ cm^{-3}. A cap layer was also grown at a thickness of 50 nm and doped at $2x10^{18}$ cm^{-3} to allow the ECV technique to fully resolve the first layer.

The SIMS depth profile was achieved in the EVA 2000 quadrupole SIMS instrument. $^{16}O_2^+$ primary ions were used with a probe energy of 4 keV at normal incidence, giving a superior depth resolution for ultrathin boron spikes in Si [10]. The erosion rate was determined by measuring the SIMS crater with a surface profilometer (Sloane Dektak Auto II).

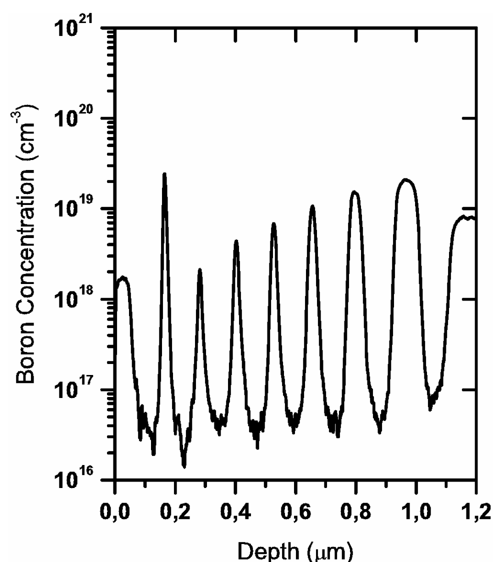

Fig. 1 SIMS profile of ultrathin boron spikes in Si (#33/9). $^{16}O_2^+$ primary ions at 4 keV were used at normal incidence.

The structure (#33/9) was employed to investigate the capability of SR depth profiling technique. A bevel of 10' was prepared using standard procedures and raw SR data were acquired by using specially prepared probes for high-resolution SR analysis [11]. The raw data were then converted into a resistivity profile using the sampling volume correction factors. The algorithm used to calculate the correction factors was also selected on the basis of previous experience with the structures having sharp doping transitions [11]. Prior to use of the correction factors the data were smoothed using the best algorithm currently available for this application. Finally the resistivity profile was converted to a carrier concentration profile using standard conversion data.

In this study, a computer-controlled ECV profile plotter (the BioRad profiler PN4300) was employed to measure the real and imaginary parts of admittance and their differentials, which were stored as raw data for every etch step. After each etch profile, the etched area size and the depth of the crater were determined with a travelling microscope and a surface profilometer, respectively. These measurements were then combined with the raw data and total current passed to obtain the carrier concentration profiles as a function of depth in series and parallel models, where the actual capacitance is connected to a series resistance in the former and a parallel resistance in the latter. The electrochemical cell contained standard carbon and calomel electrodes for anodic dissolution and reference, respectively. The sample was held against a PVC sealing ring with an approximately 1 mm of contact diameter, by using spring loaded sharp pins providing an essential ohmic back contact. The admittance behaviour was monitored with a Pt electrode. A measurement frequency of 3.2 kHz, etch voltage of 2V and etch steps of 5nm were applied. The static *I-V* and *C-V* measurements were performed prior to the etch

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profiles to establish ohmic contact integrity (<3 ohms), to examine the behaviour of the sample/electrolyte barrier, and to select optimum bias conditions.

Three different electrolytes in the literature have been employed for the ECV measurements for both models [12]. The electrolytes used in this study are 0.1 M solution of $NH_4F.HF$, 1M/0.05 solution of M NaF/H_2SO_4 and 0.1 M/0.25 M solution of NaF/Na_2SO_4 (with a pH of 4.7 by adding 2M solution of H_2SO_4) and, designated as E1, E2 and E3 respectively hereafter.

3 Results and Discussion

Fig. 1 shows a SIMS profile of the structure #33/9. The areal densities and thicknesses at FWHMs obtained from SIMS profile along with intended thicknesses are given in Table 1. It can be seen that thicknesses of the layers as indicated by the FWHMs are close to the intended values for the thick layers but are overestimated for the narrower spikes due to the intermixing effects [5]. Another feature observed from the SIMS profile was that the peak height of the spikes doped at $2x10^{19}$ cm^{-3} apparently decreased with decreasing spike width. By using the sheet densities obtained from the SIMS and intended thicknesses, peak heights can be determined in the range of $1.8{\pm}0.3x10^{19}$ cm^{-3}. Observed decrease in the peak heights with spikes width is associated with the limitation in depth resolution of SIMS, as expected.

Table 1 Intended thicknesses and FWHMs of ultrathin boron layers in Si obtained from the SIMS profile and, sheet densities obtained from SIMS, ECV and SR profiles.

Boron layers	Intended thicknesses (nm)	FWHM SIMS (nm)	Sheet densities $x10^{13}$ (cm^{-2}) SIMS	ECV	SR
Delta		9.6	2.67	2.5	11
1st	2	12.1	0.32	0.34	0.04
2nd	4	13.6	0.73	0.91	0.11
3rd	8	15.4	1.23	1.4	0.19
4th	16	20.3	2.37	2.1	0.88
5th	32	32.3	5.55	5.9	19
6th	64	68.0	13.8	15	48

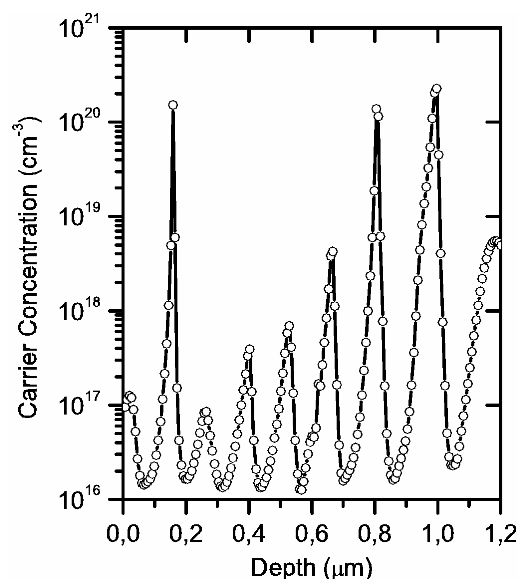

Fig. 2 SR profile of the structure (#33/9).

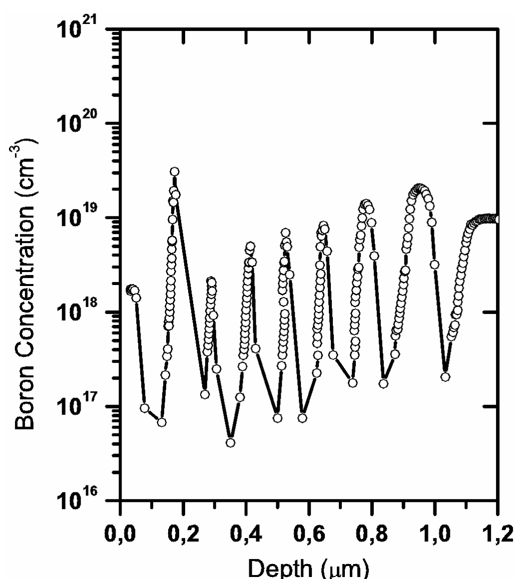

Fig. 3 ECV carrier concentration-depth profile of the structure (#33/9) obtained with electrolyte E2 at V_{meas} = - 0.6V.

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In Fig. 2, a SR profile of the structure is given where depth increment between data points was 6.6 nm. To our knowledge, SR profiles of such ultrathin layers grown by MBE have not been realised by other research groups and reported here for the first time. The reason to this might be crystalline quality as crystalline imperfections increases the noise level significantly in SR profiles [13]. It must however be noticed that all spikes are broader in the SR profile than they are in reality due to carrier spilling, which for SR occurs in the opposite direction to that in bulk material due to the presence of a bevel. Carrier spilling effects are therefore the principle limitation in such ultrathin structures. It is also clear that the doping levels are inaccurate by up to a factor of 10 times, probably indicating the limitations of existing algorithms for such layers. Sheet densities obtained from the SR profile are also given in Table 1, indicating SR is not capable of determining sheet densities correctly for such ultrathin layers. However the locations of the layers are reasonable well determined.

Fig. 3 shows an ECV depth profile of the structure. One feature is that background level is not reached due to the Debye Length exceeding the spacing between spikes. Distortions on the leading edges are observed, which increase at higher measurement voltages. This could be due to transition of etching through the change in doping level as discussed in [14]. These distortions may also result from parasitic series resistance, which may originate from conduction through the partially depleted barrier layers or from the doped region as surface states are drawn closer to it through etching [15]. Lower measurement voltages cause discrepancies between two models. Although the actual doping levels for each boron layers (except the delta layer) are about $2x10^{19}$ cm^{-3}, doping heights in the ECV profile are close to those of the SIMS profile, which as with SIMS, due to limited depth resolution. The range of applicability of ECV technique to highly spatially confined carrier systems and heterostructures can be extended by reducing the diode area, which however requires the use of photo-lithographic techniques [16].

Sheet densities obtained from this profile are presented in Table. Due to the high etch current, electrolyte E1 is not suitable for small etch steps to fully resolve such thin layers. For etch steps smaller than 5 nm, even electrolyte E2 is not practical due to very short etch time (<1 sec) which is not well controlled. In order to obtain smaller etch steps, as successfully used for rather thick layers and lower doping levels [17], diluted electrolyte E2 caused further distortions, with increased loss of Schottky barrier quality with dilution. Lower current density of electrolyte E3 for etching process is an advantage over other electrolytes by providing a practical etch time. However this lead to the doping levels being overestimated. This was due to poor Schottky characteristics as indicated by high dissipation factor.

4 Conclusions

It is demonstrated that, despite distortions on the leading edges, ECV is better suited to profiling ultrathin boron layers including a delta layer in Si, compared to the SR profiling technique. As for the ECV technique, the importance of the electrolytes is also discussed with a specific example. Although the slowest etch rate was obtained by electrolyte E3, the less satisfactory Schottky barrier prohibited successful profiling. As a result electrolyte E2 is the best choice among the three electrolytes in providing both successful Schottky barrier and reasonable slow etch rate yielding correct quantitative information.

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