Extended Abstracts of the 22nd (1990 International) Conference on Solid State Devices and Materials, Sendai, 1990, pp. 349-351

C-7-7

Sharp Boron Spikes in Silicon Grown at Reduced Pressures by Fast-Gas-Switching-CVD

A.T. Vink, P.J. Roksnoer, J.W.F.M. Maes, C.J. Vriezema and P.C. Zalm
Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands

Abstract
Boron-doping spikes in Si have been grown by fast-gas-switching CVD at 800/850°C using Si_2H_6 and B_2H_6 in 0.03/0.1 atm H_2 carrier gas. The B_2H_6 doping gas was added for 2 s by two methods, namely during growth, or as a flush while the Si_2H_6 was interrupted. High Resolution SIMS analysis has revealed the sharpest as-measured SIMS dopant profiles reported for Si grown by deposition from the gas phase. Peak B concentrations up to 5.10^{21} cm^{-3} were achieved. Electrical measurements show, that for B-spikes having a FWHM value of 5nm a sheet resistivity as low as 580 Ohm/□ can be reached.

I. INTRODUCTION

Future generations of Si-based devices will require control of composition and thickness of individual layers down to even an atomic scale. With growth techniques like MBE [1)] and UHV-CVD [2)], operating at very low temperatures and deposition pressures, examples of such control have already been given. With Low-Pressure CVD [3)] and "Limited Reaction Processing" (LRP) [4,5)] sharp transitions in doping or composition have also been reported. In LRP (a form of rapid thermal processing) changes in composition are brought about by fast thermal cycling of the substrate, while the reactant gases are changed when the substrate is cool. One can, however, also keep the substrate at constant temperature and change the reactants sufficiently fast. One may callthis "Fast Gas-Switching CVD", FGS-CVD. This fast switching of reactants is a well-known procedure in MOVPE of III-V compounds. Here control of composition on an atomic scale has been demonstrated, even in reactors operating at atmospheric pressure [6)]. Critical points in the construction of such reactors have been discussed in some detail [7)]. Here we illustrate the capabilities of FGS-CVD for Si, like in refs 2-5 using boron doping as an example.

II. EXPERIMENTAL

Our growth system is schematically shown in Fig.1. It was originally designed and used for the growth of III-V compounds, a.o. quantum wells and superlattices of (Al,Ga)As. In the turbo-pumped fast-entry lock the substrate and 40 mm diameter susceptor are heated to about 120 °C to reduce water. Via a transfer chamber, flushed with dry nitrogen, substrate and susceptor are then put into the quartz reaction chamber. The susceptor is rf-heated. The fast-switching gas system includes pressure balancing between the vent and run lines. As reactant gases Si_2H_6 and B_2H_6 diluted in palladium-diffused H_2 carrier gas (5 SLM) were used. Much care was taken to keep the water and oxygen levels low. We estimate these to be $\lesssim 0.01$ ppm of the carrier gas in most runs. Typical epitaxial growth conditions were: 800°C, 0.03 atm H_2 or 850°C, 0.1 atm H_2 and 10^{-5} to 10^{-4} atm Si_2H_6. The B_2H_6 pressure ranged from about 10^{-9} to 10^{-6} atm. At 0.03 atm some growth enhancement is observed, due to a weak plasma, but influence on the B incorporation is not expected [8)]. The B doping spikes were grown by two methods. (1): Add B_2H_6 for 2 seconds while growing Si at a rate of about 0.3 nm/s. (2): Interrupt the Si_2H_6 flow, hence the Si-epitaxy, and "flush" with B_2H_6 during this period. No essential differences in results were found under the same growth conditions. The 1000 Ωcm B-doped (100) Si substrates were cleaned using a H_2SO_4/H_2O_2 treatment, followed by a HF dip and a rinse in H_2O. After loading, a prebake was performed at 1050°C for 5 to 30 min in 1 atm H_2. With SIMS no B spike at the substrate-epilayer interface was observed with this prebake, cf ref. 9. All layers had a mirror-like appearance. To assess the doping profiles a CAMECA IMS-3F SIMS instrument was used under several experimental conditions. For optimum depth resolution a 2 keV O_2^+ primary ion beam was chosen, with an angle of incidence of 60° relative to the surface normal. Gauge implantations of ^{11}B in Si were taken to calibrate the concentration scale. At very high concentrations one may expect a reduced accuracy due to matrix effects. Therefore, additional B analyses on 2μm thick epilayers were made by Auger Electron Spectroscopy (AES), Electron Microprobe Analysis (EPMA) and Elastic Recoil Detection (ERD, see ref.10). Results of these four comparative analyses are given in Table 1. The agreement is excellent. To investigate structural damage at high B concentrations RBS was used. Electrical characterization was by Hall effect measurements on 8 x 8 mm^2 samples (including substrate) on which contacts of eutectic InGa were applied.

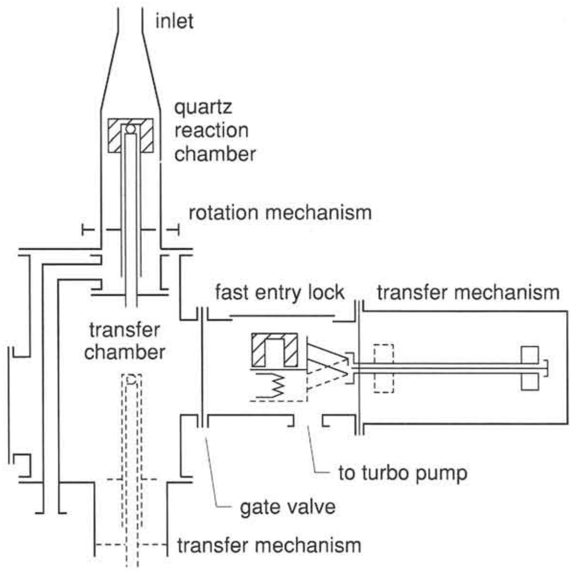


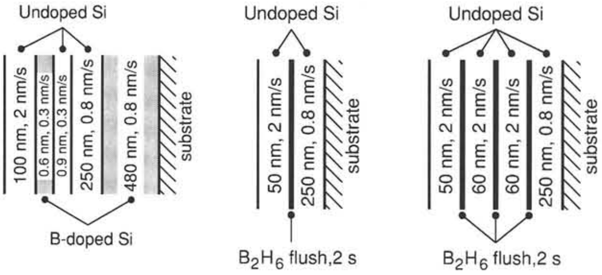
Fig. 1. Schematic drawing of the growth system, showing the fast entry lock, transfer- and reaction chamber. Susceptor transport is by mean of a horizontal and vertical transport system

Table 1. Comparison of analytical results for B

Sample	Tgrowth	Structure	Hall effect, 300 K		B concentration, cm^{-3}			
	°C		P, cm^{-3}	μ, cm^2/Vs	SIMS	AES	EPMA	ERD
427	800	2 μ epi	1.8 10^{20}	24.1	5.3 10^{20}	5.5 10^{20}	5.3 10^{20}	5.5 10^{20}
419	850	2 μ epi	2.3 10^{20}	23.4	7.5 10^{20}	9.3 10^{20}	8.2 10^{20}	9.5 10^{20}
428	800	2 μ epi	3.5 10^{20}	17.1	1.3 10^{21}	1.25 10^{21}	1.3 10^{21}	1.25 10^{21}
439	800	spike	-	-	1.8 10^{15} cm^{-2}	-	-	1.6 10^{15} cm^{-2}

III. SIMS PROFILES OF DOPING SPIKES

In Fig.2 the basic doping structures reported on are shown. First, structures were designed to assess the typical doping capabilities of our CVD system. These contain a B doped "bulk" layer of about 500 nm thickness followed by a B spike in otherwise unintentionally doped Si, see Fig 2a. In Fig. 3 some results are shown. It is seen that well defined B doped layers and sharp concentration profiles are readily obtained. We also found, however, that sub-ppm traces of water or oxygen reacting with the B_2H_6 may cause a decrease in profile sharpness. An example of this effect is the dashed spike in Fig. 3. Such reactions may also cause the increase in B concentration in the bulk layer of Fig. 3.



a b c

Fig. 2. Basic B-doping structure for "bulk" layers and spikes

In subsequent series, single and triple B spikes were grown without a preceding B doped bulk layer. In Fig. 4, SIMS profiles of a triple spike with a peak B concentration of 4.10^{19} cm^{-3} and single spikes with much higher peak concentrations are shown, all grown at 800°C. Their growth structures are given in Figs. 2b and 2c. In Table 2, the results of the SIMS measurements on these (and other) spikes are summarized. The as-measured leading inverse slopes are as steep as 1.3 to 3.7 nm/decade, while most trailing inverse slopes are 5 to 6 nm/dec.. We have established, that the trailing edge of 5 nm/dec. is affected by the SIMS measurement; the same will hold for a leading edge of 1.3 nm/dec. For sample 432, it is improbable that solid state B diffusion causes the 3 nm/dec. leading edge. This implies that under these growth conditions still sharper spikes are feasible. The tails and shoulders towards the surface in Fig. 4 depend on the actual growth conditions and are ascribed to surface segregation of various B-species and possibly some auto-doping.

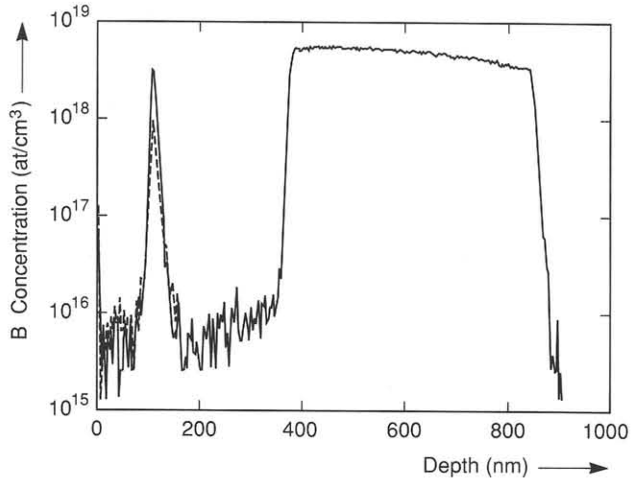


Fig. 3. SIMS B profile (5.5 keV O_2+ ions, 350 x 350 μm^2 raster, analysed area 60 μm diameter) of a structure grown at 800°C according to Fig. 2a. The B_2H_6 pressure during the growth of the 500 nm layer and spike was 1 and 4.7 10^{-9} atm, respectively. Inaccuracies in the depth and concentration scale are about +/- 5 and +/- 10% respectively.

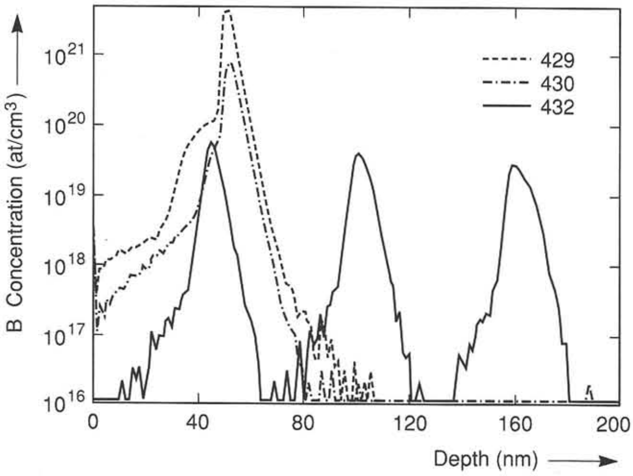


Fig. 4. SIMS profiles (2.0 keV O_2 $^+$ ions, 350 x 350 μm^2 raster, analysed area 32 μm diameter) of single and triple spikes grown according to Fig. 2b and 2c. See also Table 2. SIMS accuracies as in Fig. 3, but at high concentrations probably less.

Table 2. Hall effect (300K) and SIMS data on single doping spikes

SAMPLE	GROWTH	PB_2H_6	Electrical properties				SIMS analysis				
	TEMP.		TOTAL STRUCTURE (substrate + epilayer + spike)			SPIKE	B concentrations		Inverse slopes		FWHM
	°C	Atm.	Sheet res. (Ω/□)	Mobility (cm^2/Vs)	Holes-dose (cm^{-2})	Sheet res. (Ω/□)	Peak (cm^{-3})	Dose (cm^{-2})	leading nm/dec	trailing nm/dec	nm
432	800	2.10^{-8}	1099	70	$8.0\ 10^{13}$	3830(a)	$3.0\ 10^{19}$(a)	$2.8\ 10^{13}$(a)	2.8-3.3	4.9-5.7	5.2-7.8
423	800	2.10^{-8}	1604	96	$4.1\ 10^{13}$	1965	$4.1\ 10^{19}$	$3.2\ 10^{13}$	3.7	7.5	5.6
431	850	1.10^{-7}	1354	80	$5.7\ 10^{13}$	1500	$1.2\ 10^{20}$	$7.0\ 10^{13}$	3.0	4.9	4.7
439	850	4.10^{-7}	795	96	$1.4\ 10^{14}$	840	$8.5\ 10^{20}$	$5.5\ 10^{14}$	1.9 (b)	6.4	6.5
429	800	1.10^{-7}	548	63	$1.8\ 10^{14}$	580	$8.0\ 10^{20}$	$4.4\ 10^{14}$	2.2 (b)	5.0	4.4
430	800	5.10^{-7}	550	46	$2.4\ 10^{14}$	585	$4.6\ 10^{21}$	$2.5\ 10^{15}$	1.3 (b)	4.8	4.4

(a) average for one spike in this sample containing three spikes.
(b) steep, high concentration part.

IV. HALL EFFECT AND RBS MEASUREMENTS.

With the Hall effect, the total structure of substrate, unintentionally doped epilayer and B spike is assessed. In Table 2 the as-measured total sheet resistivity, apparent hole mobility and sheet hole concentration are given. The sheet resistivity of the spike itself is estimated from the total sheet resistivity by correcting for the conductivity of the substrate and the weakly p-type epilayer. At high B concentrations an increasing proportion of the incorporated B becomes electrically inactive, see Fig.5. The limit seems a few tenths of a monolayer, similar to the MBE-grown Sb δ-doped layers [11] also shown in Fig. 5. In agreement with these results, RBS analysis of samples 423 and 431 shows a channeling minimum yield of 3 %, while for the highest doped sample (430) channeling measurements with grazing exit angle showed a small but well defined damage peak, located at the depth of the B spike.

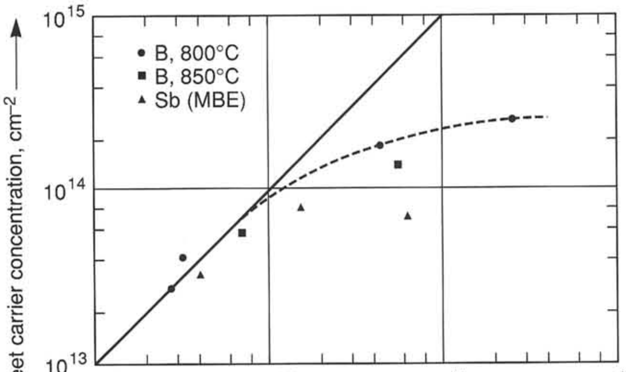


Fig. 5. Sheet hole concentration (300 K) versus sheet B concentration (SIMS) for the sample of Table 2. Data on Sb δ- doped layers, taken from ref. 11, are added for comparison.

ACKNOWLEDGEMENT.

The authors like to thank Dr. L.J. IJzendoorn for the RBS analyses, Mr. W.H. van de Wijgert for the AUGER data, Mr. J.H.T. Hengst for the EPMA results and Prof. Dr. F.H.P.M. Habraken (University of Utrecht) for the ERD analyses.

REFERENCES

1) See e.g. "Silicon Molecular Beam Epitaxy", Proceedings of the 3rd Int.Symp. on Si-MBE, Strasbourg, France, 1989.
Part A published as Thin Solid Films, Vol. 183 (1989),
Part B published as Thin Solid Films, Vol. 184 (1990).
2) B.S. Meyerson, F.K.Legoues, T.N. Nguyen, D.L. Harame, Appl. Phys. Lett. 50 (1987) 113.
3) L.Vescan, H. Beneking, O. Meyer in "Materials Issues in Silicon IC Processing", Mat. Res. Soc. Symp. Vol 71 (1986) 133.
4) C.M. Gronet, J.C. Sturm, K.E. Williams, J.F. Gibbons, S.D. Wilson, Appl. Phys. Lett. 48 (1986) 1012.
5) J.E. Turner, J. Amano, C.M. Gronet, J.F. Gibbons, Appl. Phys. Lett. 50 (1987) 1601.
6) M.R. Leijs, C. van Opdorp, M.P.A. Viegers, H.J. Thalen-van der Mheen, J. Crystal Growth 68 (1984) 431.
P.M. Frijlink, I. Maluenda, Japan. J. Appl. Phys. 21. (1982) L574.
7) C. van Opdorp, M.R. Leijs, J. Crystal Growth 84 (1987) 271.
8) J.H. Comfort, R.Reif, J. Appl. Phys. 65 (1989) 1067.
9) D.J. Robbins, A.J.Pidduck, J.L. Glasper, I.M. Young, C. Pickering, Thin Solid Films 183 (1989) 299.
10) C.P.M. Donselman, W.M. Arnold Dik, F.H.P.M. Habraken, W.F. van der Weg, MRS Bulletin 12 (1987) 35.
11) A.A. van Gorkum, K. Nakagawa, Y. Shiraki, J. Appl. Phys. 65 (1989) 2485, and private communication.