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Remarks on the room temperature impurity band conduction in heavily Al⁺ implanted 4H-SiC

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The processing parameters which favour the onset of an impurity band conduction around room 10 temperature with a contemporaneous elevated p-type conductivity in Al⁺ implanted 4H-SiC are 11 highlighted by comparing original and literature results. In the examined cases, Al is implanted at 12 300-400 °C, in concentrations from below to above the Al solubility limit in 4H-SiC 13 $(2 \times 10^{20} \text{ cm}^{-3})$ and post implantation annealing temperature is $\geq 1950 \,^{\circ}\text{C}$. Transport measurements 14 feature the onset of an impurity band conduction, appearing at increasing temperature for increas-15 ing Al implant dose, until this transport mechanism is enabled around room temperature. This con-16 dition appears suitable to guarantee a thermal stability of the electrical properties. In this study, the 17 heaviest doped and less resistive samples (Al implanted concentration of 5×10^{20} cm⁻³ and resis-18 tivity of about $2 \times 10^{-2} \Omega$ cm) show a carrier density above the Al solubility limit, which is con-19 sistent with at least a 50% electrical activation for a 15% compensation. The model of Miller and 20 Abrahams well describes the resistivity data of the lower doped sample, whereas a deviation from 21 the behaviour predicted by such a model is observed in the higher doped specimens, consistent 22 23 with the occurrence of a variable range hopping at low temperature. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4926751]

24 INTRODUCTION

Ion implantation is the most used technology for obtain-25 26 ing planar selective area doping and impurity doping concen-27 tration far above the solid solubility limit in semiconductor materials for electronic device applications and for funda-28 mental studies. Aluminum (Al) is the preferred acceptor dop-29 ing species in SiC when very low p-type resistivity values 30 31 are desired. To the best of the authors' knowledge, and only for demonstration purposes, the maximum implanted Al con-32 centration in the p-type emitters of SiC p-i-n diodes has been 33 1.5×10^{20} cm⁻³, see, for example, Refs. 1–3. In general, an 34 increase of the semiconductor doping is desired in the device 35 contact areas for reducing the contact resistance. 36

The state of the art on the electrical activation of implanted 37 Al in 4H-SiC is hereafter resumed. For a given implanted Al 38 concentration, the p-type doping increases with the increase of 39 the post implantation annealing temperature, while for a fixed 40 post implantation annealing temperature, the p-type doping 41 increases with increasing implanted Al concentration. 42 Maximum doping values have been obtained for 1950-2100 °C 43 annealing with conventional^{4,5} and microwave heating.^{2,3} 44 Minimum room temperature (RT) resistivity values of few 10^{-2} 45 Ω cm, which are good for sheet resistance values $<10^4 \Omega/\Box$, 46 47 have been obtained by implanted Al concentrations above the solubility limit of 2×10^{20} cm⁻³,⁶ and post implantation anneal-ing temperatures ≥ 1950 °C.^{4,5,7} The characterization of the hole 48 49 transport in such low p-type resistivity Al implanted 4H-SiC 50 materials allow us to hypothesize that implanted Al concentra-51 tions above 1.5×10^{20} cm⁻³ could be used for the fabrication of 52 highly conductive p-type paths in high temperature SiC sensors, 53

or for designing new current collection geometries in SiC power 54 devices. In fact, the temperature dependence of the p-type resis-55 tivity in such SiC materials features a weak temperature depend-56 ence associated to the formation of an impurity band (IB) 57 conduction around room temperature,^{2-4,8,9} which guarantee p-58 type SiC materials of almost stable transport features in a wide 59 large temperature range around RT. It is worthwhile to remem-60 ber that for dopant concentration below the 10^{20} cm⁻³ decade, 61 the high thermal ionization energy of every dopant species in 62 SiC is responsible of a strong temperature dependence of the 63 SiC transport properties due to carrier freeze-out effects, see, for 64 example, Refs. 10 and 11. 65

The aim of this article is to highlight the identification of the 66 processing parameters which favour the onset of an impurity 67 band conduction around room temperature joined to an elevated 68 p-type conductivity in Al⁺ implanted 4H-SiC. Both original and 69 literature data are used for this purpose. Moreover, details on the 70 transport data that support the identification of the IB transport 71 mechanism in samples of different Al implant concentrations are 72 discussed, by claiming the role of such a mechanism in obtaining 73 very low resistivity values and a carrier density that are nearly 74 temperature independent around RT. For one of the heavier 75 doped samples, the consistency of the low temperature conduc-76 tivity data with the Mott law was evidenced, suggesting the onset 77 of a variable range hopping transport at low temperature. 78

SAMPLE PROCESSING AND MEASUREMENTS

The discussion of the transport properties of Al⁺ heavily 80 implanted 4H-SiC samples takes off from two widely recog-81 nized observations: (i) the increase of the post implantation 82

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annealing temperature leads to a more efficient electrical
activation of the implanted Al impurities^{2,4,8} and (ii) the
increase of the activated Al concentration shifts towards
higher temperatures, the onset of a hole conduction through
impurity states.^{8,10}

This work, following the result (i), takes into account 88 only samples annealed at the maximum reachable tempera-89 tures of 1950 °C and 2000 °C by an inductively heated fur-90 nace⁴ and by microwave heating,⁷ respectively. Moreover, to 91 discuss benefit effects of the result (ii), samples of implant 92 concentration above $1 \times 10^{20} \text{ cm}^{-3}$ are accounted for, in the 93 range $1.5 \times 10^{20} - 5 \times 10^{20} \text{ cm}^{-3}$. In fact, samples with Al 94 implanted concentration below $1 \times 10^{20} \text{ cm}^{-3}$, although sub-95 mitted to the 1950 °C-2000 °C thermal treatments, exhibit a 96 significant carrier freeze-out into impurities in a wide range 97 of temperatures, where an electrical transport in valence 98 band states (VB) is recognizable.¹⁰ Features of an IB trans-99 port appear, in these samples, only by decreasing enough the 100 temperature of measurement. The use of implanted Al con-101 centrations above 1×10^{20} cm⁻³ and 1950 °C–2000 °C 102 annealing has the effect to enhance the acceptor density, to 103 104 shift the onset of the impurity band conduction towards RT and to avoid a temperature region dominated by carrier 105 freeze-out. This condition has been effectively seen for Al 106 implanted concentrations $\geq 3 \times 10^{20} \text{ cm}^{-3.4}$ It is worthwhile 107 to notice that such a density is higher than the Al solubility 108 limit in 4H-SiC at 2000 °C, 2×10^{20} cm⁻³.⁶ 109

The samples here investigated are in part a selection 110 from previous studies and in part new processed specimens, 111 all that with the purpose to obtain an homogeneous set of 112 113 identical Al⁺ implanted 4H-SiC with 1950 °C-2000 °C post implantation annealing obtained by the two mentioned heat-114 ing methods, conventional and microwave. Possible effects 115 of different implant temperatures 300 °C and 400 °C were 116 also inquired. Table I summarizes the sample set of this 117 study together with their processing parameters, which are 118 detailed in the following. 119

High purity semi-insulating, 8° off-axis $\langle 0001 \rangle$ 4H-SiC wafers were Al⁺ implanted with different energy and dose values to obtain almost box shaped Al depth profiles next to the wafer surface. A Tandentron 1.7 MV accelerator (High Voltage Engineering Europa B.V.) and 3 inches hot holder for sample mounting and heating were used. During implantation, the SiC samples were covered by a thick SiO₂ film and kept at 300 °C or at 400 °C. More precisely, samples 127 used for previous studies were implanted at 400 °C, while 128 the original samples of this study have been implanted at 129 300 °C. Implantation schedules were decided by using 130 SRIM2008 simulations¹² and verified by Secondary Ion 131 Mass Spectroscopy (SIMS) on few samples. Homogeneous 132 Al concentrations of 1.5×10^{20} , 3×10^{20} , and 5×10^{20} cm⁻³ 133 were obtained across a thickness of about 400 nm. The 134 implanted wafers were diced into pieces of $5 \text{ mm} \times 5 \text{ mm}$ for 135 facilitating van der Pauw (vdP) Hall measurements. These 136 pieces were annealed at 1950 °C/5 min in a conventional 137 inductively heated furnace ("conventional annealing" CA) or 138 at 2000 °C/30 s in a microwave heating system ("microwave 139 annealing" MWA). Details about these CA and MWA sys- 140 tems and their characteristic temperature versus time cycles 141 are provided in Refs. 2, 7, 13, and 14. During CA and MWA, 142 the implanted sample surface was protected by a carbon film 143 (C-cap), which was obtained by a 900 $^{\circ}$ C/2 min pyrolysis in 144 forming gas of a 2–4 μ m thick resist film.¹⁵ Before the spin- 145 ning of the resist film, the SiC native oxide was etched away 146 in a hydrofluoric acid bath and samples were dried in nitro- 147

gen at 110 °C for 30 min. After CA and MWA, C-cap was 148 removed by 850 °C/15 min dry oxidation. Root mean square 149 (rms) surface roughness after C-cap removal was measured 150 by Atomic Force Microscopy in the tapping mode on a few 151 samples and found to be in the range of 0.5–4.7 nm.⁵ 152

It is widely accepted that the implanted Al does not diffuse during post implantation annealing.^{9,16} This has been 154 assumed true for all the samples of this study, which is an 155 approximation. Such an approximation is corroborated by 156 the fact that the measured Hall hole density always increases 157 with the implanted Al concentration, even when this latter 158 increases above the solubility value. Moreover, Hall hole 159 densities overcoming the Al solubility value are effectively 160 measured as it was shown in previous reports^{2–5} and will be 161 recalled here in the "Results and Discussion" section. 162

Square van der Pauw (vdP) devices have been obtained 163 by fabricating triangular ohmic contacts on the four corners 164 of each 5 mm \times 5 mm annealed samples. For ohmic contacts, 165 sputtered Ti(80 nm)/Al(2% Si, 350 nm) films alloyed at 166 1000 °C for 2 min in vacuum have been used. Due to the 167 non-negligible dimensions of the contacts compared to the 168 device size, correction factors have been applied to the 169 results of electrical measurements as suggested in Ref. 17. In 170

TABLE I. Process parameters of the AI^+ implanted p-type 4H-SiC samples of this study. From left to right, the column content is: sample label with, if the case, citation of previous articles where the same sample has been used, simulated implanted Al concentration by SRIM2008,¹² implantation temperature, measured as-implanted Al concentration by SIMS, post implantation annealing type (CA and MWA) with temperature and time, RT Hall hole density, and RT resistivity.

Sample	Nominal (SRIM2008) implanted Al density (cm ⁻³)	Implant temp. (°C)	Measured (SIMS) implanted Al density (cm ⁻³)	Post implantation annealing		RT Hall hole density (cm^{-3})	RT resistivity (Ω cm)
305g ^{2,3}	$1.5 imes 10^{20}$	400	n. m.	MWA	2000 °C/30 s	2×10^{19}	0.067
305b	$1.5 imes 10^{20}$	400	n. m.	CA	1950 °C/5 min	7×10^{18}	0.097
294c ^{2,3,7}	$3 imes 10^{20}$	400	2.94×10^{20}	MWA	2000 °C/30 s	$5 imes 10^{19}$	0.056
293a	$3 imes 10^{20}$	300	2.94×10^{20}	MWA	2000 °C/30 s	$5 imes 10^{19}$	0.059
293e	$3 imes 10^{20}$	300	2.94×10^{20}	CA	1950 °C/5 min	$5 imes 10^{19}$	0.052
296c	$5 imes 10^{20}$	300	5.34×10^{20}	MWA	2000 °C/30 s	$3.5 imes 10^{20}$	0.023
296e	$5 imes 10^{20}$	300	5.34×10^{20}	CA	1950 °C/5 min	1.4×10^{20}	0.032

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the samples of this study, such a correction resulted to 171 increase the resistivity experimental data of a few percent 172 (1%-4%); while more significant was the correction to the 173 Hall voltage, which led to Hall hole values of about 174 10%–30% lower than the rough experimental values, 175 depending on the contact pattern. It is worth noticing that 176 this clarification supports the electrical quality of the samples 177 here discussed, in fact, the correction guarantee that the 178 reached conductivity values are not apparently enhanced by 179 contact geometry. Four point vdP Hall measurements have 180 been performed at the temperature range of 30-680 K and 181 0.8-1 T variable magnetic field. In the samples of this study, 182 Hall hole densities from $7 \times 10^{18} \text{ cm}^{-3}$ to $1 \times 10^{21} \text{ cm}^{-3}$ 183 have been obtained. The feasibility of the conversion of 184 "Hall hole density" into "drift hole density," which is the 185 true value of free carriers, through the introduction of the r_H 186 Hall factor will be critically discussed. 187

188 RESULTS AND DISCUSSION

Figures 1(a) and 1(b) compare the temperature depend-189 ence of the Hall hole density and Hall hole mobility in two 190 samples with identical $3 \times 10^{20} \text{ cm}^{-3}$ Al implanted concen-191 tration and identical 2000 °C/30 s MWA but different im-192 plantation temperatures: 300 °C and 400 °C, samples 294c 193 and 293a of Table I, respectively. The curves of the two sam-194 ples are identical within the experimental error. This result 195 allows us to assume that a 100 °C reduction of the implanta-196 tion temperature, from 400 °C to 300 °C, does not affect the 197 quality of the subsequent post implantation annealing pro-198 cess; therefore, it allows us to compare the results of the 199 transport measurements of all the samples of Table I, inde-200 201 pendently of their implantation temperature.

Figures 2(a) and 2(b) depict the temperature dependen-202 ces of the Hall hole density and Hall mobility for all the dif-203 ferent implanted Al concentrations of the samples of Table I 204 and the different post implantation annealing: 1950 °C/5 min 205 CA (closed symbols) and 2000 °C/30 s MWA (open sym-206 bols). For sake of precision, it can be added that Figs. 2(a)207 and 2(b) contain all the samples of Table I except 294c. The 208 curves of Figs. 2(a) and 2(b) show that for identical 209 implanted Al doses, the MWA samples compared to their 210 CA counterparts show a generally higher carrier density and 211 212 a correspondingly lower mobility, while keeping very similar trends of temperature dependence. The major physical differ-213 ence between conventional and microwave heating may be 214 an interaction between the microwave field and the free car-215 216 riers in the implanted layer, the more the electrical activation of the implanted dopant proceeds. Such an effect could be 217 tested if identical CA and MWA thermal cycles could be 218 219 compared, but presently this is not possible because of the technical constrains of the two annealing set-ups. In this sit-220 uation, the differences between the correspondent CA and 221 MWA curves of Figs. 2(a) and 2(b) are ascribed to the 50 °C 222 223 higher temperature of the MWA compared to the CA. Hereafter, the features of the curves of Figs. 2(a) and 2(b)224 will be discussed only with respect to the value of the 225 implanted Al concentration. 226



FIG. 1. Comparison of (a) the Hall hole density and (b) the Hall hole mobility for 3×10^{20} cm⁻³ Al⁺ implanted and 2000 °C/30 s MWA 4H-SiC samples, which are different only for the implantation temperature: (close symbols) 300 °C and (open symbols) 400 °C. The experimental data were corrected for contact size systematic error (see text).

Temperature (K)

Only the 1.5×10^{20} cm⁻³ Al implanted specimens have 227 an Arrhenius plot of the Hall hole density data where an ex- 228 ponential trend is observable (see Fig. 2(a)), which is typical 229 for the carrier transport through valence band states in the 230 hole freeze-out regime. Such a trend takes place above about 231 200 K and it is consistent with an acceptor thermal ionization 232 energy of about 100 meV, in agreement with the conclusions 233 of Ref. 10. The temperature (T) dependence of the corre- 234 spondent mobility curves (see Fig. 2(b)) shows a trend 235 almost equal to $T^{-3/2}$ that is typical of phonon scattering. 236 This result says that the crystalline quality of these implanted 237 and annealed 4H-SiC specimens is preserved in spite of an 238 implanted Al concentration approaching the solubility value. 239 Notwithstanding this, a fitting of the Hall data was not per- 240 formed, because the model for transport discussed in Ref. 10 241 is reliable below an acceptor density of 10^{20} cm⁻³. For tem- 242 peratures lower than 200 K, the data of this CA sample show 243 the hint of a minimum in the Hall density curve with the cor- 244 respondent mobility data decreasing more abruptly than the 245 typical trend expected for ionized impurity scattering, the 246 latter having a $T^{3/2}$ temperature dependence or weaker. 247 These features are generally recognized as due to the onset 248 of a impurity band conduction, which prevails at low temper- 249 atures, whereas around the Hall density minimum a mixed 250 carrier transport takes place between IB and VB states, as 251 reviewed, e.g., by Mott in Ref. 18. The theoretical Hall den- 252 sity and mobility curves depicted in Ref. 10, however, show 253

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FIG. 2. Temperature dependence of: (a) the Hall hole density and (b) the Hall hole mobility of given Al implanted concentrations in 8° off-axis $\langle 0001 \rangle$ high-purity semi-insulating 4H-SiC and different post implantation annealings: CA 1950 °C/5 min (full symbols), and MWA 2000 °C/30 s (open symbols). The implanted Al concentration is shown in the inset of (a). For comparison, the trends T^{3/2} and T^{-3/2} for ionized impurity scattering and non-polar phonon scattering, respectively, are shown as dashed lines in (b). The experimental data were corrected for contact size systematic error (see text).

a departure from experimental data towards the low temperatures, yet before such a minimum, suggesting that the influence of the transport through localized states is effective at higher temperatures in respect to that of such a minimum. In the 1.1×10^{20} cm⁻³ Al implanted sample, in particular, a weak effect of the IB conduction can be presumable up to the proximity of RT.

The 3×10^{20} cm⁻³ and 5×10^{20} cm⁻³ Al implanted 261 specimens show a weak temperature dependence of the Hall 262 hole density values, weaker for higher implanted Al concen-263 264 trations, and broad minima centred at about room temperature and above room temperature for the lower and higher 265 implanted Al concentration, respectively (see Fig. 2(a)). The 266 sign of the Hall coefficient was that expected for positive car-267 riers at any temperature. The correspondent mobility values 268 have a temperature dependence dominated by an almost flat 269 trend at high temperature and a steep decrease with decreasing 270 temperature, as for the $1.5 \times 10^{20} \text{ cm}^{-3}$ Al implanted samples 271 (see Fig. 2(b)). In the light of the global trends of all the sam-272 ples, the occurrence of a mixed conduction where the trans-273 port through impurity states is relevant at any temperature has 274 275 been hypothesized. The possibility to observe a significant IB

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conduction at so high temperatures like room temperature and 276 above is not usual and it is possible in p-type 4H-SiC, owing 277 to the high thermal ionization energy of the Al acceptors. An 278 IB conduction around room temperature has been previously 279 reported in 4H-SiC for a much higher Al implanted concentra- 280 tion of 1.5×10^{21} cm⁻³, where the samples were implanted at ²⁸¹ comparable temperature than in the present study but annealed 282 at a much lower temperature (1600 °C/10 min).⁸ Major differ- 283 ences between the results of this study and those of Ref. 8 are 284 a higher hole density, higher mobility, and lower resistivity 285 values in the former. These differences can be justified by a 286 more efficient activation of the implanted dopant in this work, 287 thanks to the higher annealing temperatures, 1950 °C–2000 °C 288 against 1600 °C. This result must be highlighted, because it 289 indicates that these extreme annealing processes permit to 290 reach a high enough acceptor density to induce a significant 291 IB conduction around RT at lower implant dose in respect to 292 Ref. 8, without detrimental effects on the mobility, which, on 293 the contrary, is favoured probably by a lower amount of lattice 294 disorder. 295

The estimation of the electrical activation (the fraction 296 between dopant density in substitution positions and 297 implanted dopant density) of a given post-implantation 298 annealing process is generally possible if the transport of car- 299 riers takes place in the extended state band (VB), although 300 the need of the Hall factor correction, r_H , which converts 301 Hall into drift data, to avoid systematic inaccuracies, must be 302 highlighted. In Ref. 10, it has been shown that this evaluation 303 is reliable by fitting the data in the relaxation time approxi- 304 mation (RTA), till a maximum Al implanted concentration 305 of $1.12 \times 10^{20} \text{ cm}^{-3}$, by adopting an empirically obtained 306 Hall factor for Al doped p-type 4H-SiC.¹⁹ In such p-type 307 samples, the Hall factor must account for the occupancy of 308 both the heavy and light hole valence bands and their anisot- 309 ropy. In fact, in the case of two parallel channels "1" and 310 "2," r_H takes the form 311

$$r_H = (p_1 + p_2)e\frac{\sigma_1\mu_{1H} + \sigma_2\mu_{2H}}{(\sigma_1 + \sigma_2)^2}.$$
 (1)

In Eq. (1), p_i , σ_i , and μ_{iH} are the hole density, the conductivity, 312 and the Hall mobility in the i^{th} conduction channel (i = 1, 2); e^{-313} is the electron charge. In the same channel of transport, the 314 Hall and *drift (true)* mobility, μ_{iH} and μ_i , respectively, are gen-315 erally different. The ratio μ_{iH}/μ_i is the *intra-valley* Hall factor, 316 r_{Hi} , which for a transport into a band of extended states (i.e., 317 the states of the valence or conduction band) can be computed 318 in the frame of the RTA. In this framework, r_{Hi} is defined as 319 the product of the scattering factor $r_{Si} = \langle \tau_i^2 \rangle / \langle \tau_i \rangle^2$ with the 320 mass anisotropy factor r_{Ai} , that is, $r_{Hi} = r_{Si}r_{Ai}$ [Ref. 20 and 321 references therein]. The scattering factor r_{Si} accounts for the ki- 322 netic energy distribution of free carriers within a given band 323 (for non-monokinetic carriers), whereas the mass anisotropy 324 factor r_{Ai} is a correction to r_{Si} due to a possible anisotropy of 325 such a band. For p-type 4H-SiC, Eq. (1) has been used in Refs. 326 10 and 20–22, with some different assumptions, to describe the 327 hole transport through the two parallel channels of the heavy 328 and the light hole valence bands for acceptor concentration in 329 the range $2 \times 10^{15} - 1 \times 10^{20} \text{ cm}^{-3}$. 330

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When a transport through an impurity band is added in 331 parallel to the transport through extended states, which, in 332 this study, is the case for the $3 \times 10^{20} \text{ cm}^{-3}$ and 333 $5 \times 10^{20} \text{ cm}^{-3}$ samples over the whole temperature range of 334 335 measurements, it is hard to apply Eq. (1) to obtain the Hall factor. In fact, the interpretation of the Hall coefficient R_H as 336 a quantity simply related to the reverse of the carrier density 337 338 (normal Hall effect) becomes doubtful for an impurity band conduction; the sign of the Hall voltage could even to be 339 inverted in this regime.^{18,23,24} In this contest, the Hall factor 340 r_H could empirically account for any deviation of the Hall 341 coefficient R_H from its normal meaning, but it could take 342 values not simply predictable. In any case, for the conduction 343 344 through localized states, the Hall factor r_H loses its usual 345 meaning because the hopping transport can be described through a thermally activated hopping probability, which 346 cannot be calculated in terms of an energy dependent relaxa-347 tion time. On the other hand, Mott suggested that in IB con-348 duction, around the transition to metal, if the Hall coefficient 349 does not have an abnormal sign, its value is not far from the 350 value expected for the carrier density.¹⁸ However, the con-351 version of the Hall values of Fig. 2(a) for the heaviest doped 352 samples in *drift* ones is not reliable and thus neither the cor-353 respondent acceptor density can be simply estimated. In spite 354 355 of this conclusion, the following qualitative analysis on the curves of Fig. 2(a) can be performed. 356

Although none of the curves of Fig. 2(a) shows carrier 357 exhaustion, the Hall hole density data of the samples with 358 the higher Al implanted concentration of $5 \times 10^{20} \text{ cm}^{-3}$ 359 360 could be used for a rough estimation of the maximum net acceptor density (acceptor density minus compensating im-361 purity density). In fact, the net acceptor density can be con-362 sidered at least equal to the experimental Hall hole density 363 measured at higher temperature, where the transport through 364 extended states is expected to be dominant and then the 365 *intra-valley* r_H factor of Ref. 19 can be tentatively assumed 366 to correct the Hall data. The 2000 °C/30 s MWA sample 367 shows a maximum Hall density at the highest temperature of 368 $3.5 \times 10^{20} \text{ cm}^{-3}$, which, if reduced of a r_H factor of about 369 0.6, is consistent with a net acceptor value of about 370 $2.2 \times 10^{20} \text{ cm}^{-3}$. This density may correspond to a 100% 371 electrical activation for about a 50% compensation, or to a 372 more than 50% electrical activation for a 15% compensation. 373 374 The latter hypothesis seems to be more reasonable in the light of the electrical activation and compensation which 375 have been obtained for Al implanted 4H-SiC samples in the 376 range 5×10^{19} -1.5 $\times 10^{20}$ cm⁻³ and 1950 °C/5 min CA: 70% 377 and 10%-13%, respectively.¹⁰ 378

A confirmation of the occurrence of a transport through 379 localized states can be inferred from the study of the temper-380 ature dependence of the implanted material sheet resistance 381 382 or the material resistivity, which is the measured sheet resistance multiplied by implanted layer thickness. No correction 383 to the implanted thickness needed to be accounted for Ref. 384 385 25, at any temperature, the surface/interface depletion of the layer being negligible (however, such a correction would 386 have the effect to reduce further the resistivity data). Sheet 387 resistance has been measured in absence of magnetic field, 388 389 even if none magneto-resistance effect has ever been



FIG. 3. Arrhenius plot of the resistivity data for all the sample of this study: (a) aro d above RT, (b) over the whole range of temperature of measurements. The implanted Al concentrations are shown in the inset of (a). Open and full symbols refer to MWA and CA samples, respectively. The vertical dashed line of (a) corresponds to room temperature. Dashed and continuous lines in (b) show the exponential trends for 20 meV and 100 meV activation energies, respectively. The experimental data were corrected for contact size systematic error (see text).

detected for the samples of this study. Figs. 3(a) and 3(b) 390 show the Arrhenius plots of the resistivity of all the samples 391 of this study, the same data are plotted on two different tem- 392 perature windows in order to clearly visualize the resistivity 393 temperature dependence around and above RT in the case of 394 Fig. 3(a), and even below RT in the case of Fig. 3(b). It is 395 evident that, for each sample, sheet resistance measurements 396 were performed until lower temperatures than those of Hall 397 measurements, whose scattering increases more and more 398 with the sample cooling. Such a scattering is due to the very 399 low values of the Hall potential at such very high carrier den- 400 sities, while the contacts preserve their ohmic behavior up to 401 10 K and the current can flow at any temperature through the 402 implanted layers because the carrier density remains high 403 thanks to the IB conduction. The sheet resistance, which 404 increases with decreasing temperature, is measurable until 405 the voltage drop at the vdP contacts does not overpasses the 406 voltage limit of the used instrument set-up. The resistivity 407 data, then obtained, show some general trends (see Figs. 3(a) 408 and 3(b)), which confirm previously published results, see, 409 as an example, Ref. 8. In particular, all the samples of this 410

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study have resistivity values that decrease with increasing 411 temperature as expected for a semiconductor material. This 412 result is consistent with the published range of 413 6.4×10^{20} - 8.7×10^{20} cm⁻³ Al concentrations for the occur-414 ring of the metal to insulator transition (MIT), which has 415 been observed in liquid phase epitaxial growth 4H-SiC mate-416 rials.²⁶ In fact, in this study, the maximum value of Al 417 implanted concentration is $5 \times 10^{20} \text{ cm}^{-3}$. It should also be 418 noted that implanted materials are expected to contain more 419 crystal disorders than the epitaxial ones. For elevated doping 420 densities, the presence of crystal disorder could favor the 421 persistence of a hopping conduction by inhibiting the MIT. 422 423 Concerning the comparison of the two annealing methods, 424 Figs. 3(a) and 3(b) show that for identical implanted Al concentration; the resistivity means MWA specimen is generally 425 lower than that of the CA, one which is attributed to a more 426 efficient electrical activation by the MWA method because 427 428 of its higher temperature. Finally, Figs. 3(a) and 3(b) show that the resistivity values decrease for increasing implanted 429 Al concentration. The minimum RT resistivity obtained in 430 the Al⁺ 4H-SiC material of this study is $2.3 \times 10^{-2} \Omega$ cm for 431 the 5×10^{20} cm⁻³ implanted Al concentration and 2000 °C/ 432 30 s MWA. This result agrees with the conclusions of Heera 433 et al.,²⁷ who calculated the values of minimum resistivity as 434 a function of the acceptor density expected for hole transport 435 through extended states in the ideal case of null compensa-436 tion and predicted that resistivity data lower than such mini-437 mum values could be obtained only by achieving a transport 438 through an impurity band. In particular, they²⁷ computed a 439 resistivity of $7 \times 10^{-2} \Omega$ cm for hole transport in valence 440 band with 5×10^{20} cm⁻³ Al concentration. 441

The transition between a carrier conduction through 442 band states to IB conduction is particularly evident in the 443 $1.5 \times 10^{20} \text{ cm}^{-3}$ Al implanted samples. In these samples, 444 both the regimes are clearly visible in a wide temperature 445 range, despite some mixed conduction effects in between. 446 Around and above room temperature (see Fig. 3(a)), the 447 Arrhenius plots of the p-type resistivity of these samples 448 show a clear exponential trend with thermal activation 449 energy of about 100 meV, which agrees with that obtained 450 451 from the data of Fig. 2(a). By decreasing temperature (see the curves of Fig. 3(b)), the resistivity Arrhenius plots of the 452 $1.5 \times 10^{20} \text{ cm}^{-3}$ samples show a transition from the high 453 temperature exponential trend to another exponential trend 454 of much lower activation energy, about 20 meV, towards 455 lower temperatures. This transition takes place in a narrow 456 temperature window around about 200 K. Such a broken-457 straight line behavior can be commented according to the 458 pioneering model of Miller and Abrahams.²⁸ This model 459 describes the temperature dependence of the conductivity in 460 semiconductor materials $\sigma(T)$ as the sum of three thermally 461 activated conduction mechanisms: σ_1 , σ_2 , and σ_3 , due to the 462 tran into extended states (valence or conduction band), 463 hopping _____ to the higher impurity Hubbard band, and 464 465 between impurity states, respectively

$$\sigma(T) = \sigma_1 + \sigma_2 + \sigma_3$$

= $\sigma_{01}e^{-\epsilon_1/K_BT} + \sigma_{02}e^{-\epsilon_2/K_BT} + \sigma_{03}e^{-\epsilon_3/K_BT}.$ (2)

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In Eq. (2), ϵ_1 , ϵ_2 , and ϵ_3 are the thermal activation of the 466 three transport mechanisms, respectively, and K_B is the 467 Boltzmann constant. Generally, the σ_1 and σ_3 contributions 468 extend over wide temperature windows, while the possibility 469 to detect the σ_2 contribution is restricted to a narrow temper- 470 ature range in between those of σ_1 and σ_3 , and limited to in-471 termediate doping conditions even depending on the 472 compensation ratio.^{29,30} A linear trend appearing in the low 473 temperature Arrhenius plot of the resistivity is, in the most 474 of the cases, attributable to a transport through a hopping 475 mechanism between an occupied dopant atom to a nearest 476 unoccupied one. Therefore, in the case of the 477 $1.5 \times 10^{20} \text{ cm}^{-3}$ sample, the $\approx 20 \text{ meV}$ activated transport 478 was attributed to a hopping conduction between nearest Al 479 acceptors. The model of this hopping mechanism predicts a 480 thermal activation energy ϵ_3 dependent on compensation and 481 doping level.^{28–31} 482

A departure from the behavior of the 1.5×10^{20} cm⁻³ 483 sample is observed in the data of the heavier doped samples, 484 of implanted Al concentration $\geq 3 \times 10^{20}$ cm⁻³, whose resistivity Arrhenius plots do not evidence any reliable straight 486 trend in the whole temperature range if accurately analyzed; 487 therefore, in their low temperature conductivity data, neither 488 the σ_2 nor the σ_3 contributions can be recognized. A similar 489 behavior has been not claimed by Heera *et al.*,⁸ who interpreted the resistivity data of all their samples, none of which 491 displayed the maximum doping level here reached, in terms 492 of the Miller and Abrahams model. 493

The ensemble of the results of this study on Al^+ 494 implanted 4H-SiC materials, instead, agrees with the experi- 495 mental results of Müller et al.³² on Al doped 6H-SiC bulk 496 materials. In fact, these authors performed temperature de- 497 pendent Hall effect measurements on samples with specific 498 resistivity in the range $1-8 \Omega$ cm. In all these samples, indi-499 cations for impurity conduction at low temperatures have 500 been found with the following major difference. In the lower 501 doped samples ($\rho > 0.2 \ \Omega \ cm$), a sharp transition between 502 impurity and valence band conduction transport was visible 503 in the temperature dependence of specific resistivity, charge 504 carrier concentration, and mobility. In highly doped samples 505 $(\rho < 0.2 \ \Omega \ \text{cm})$, the same transition was no longer confined 506 to a small temperature range and it was much less abrupt. 507 Müller *et al.*³² concluded that in their heavily Al doped bulk 508 6H-SiC, the impurity conduction was present at high temper- 509 atures so that at least two competing transport mechanisms 510 took place simultaneously. In the Al⁺ implanted 4H-SiC 511 samples of this study, a resistivity one order of magnitude 512 lower has been achieved and the phenomenon is much more 513 evident. 514

The fact that no clear exponential trend can be recognized 515 in our samples could be justified, at least partially, in terms of 516 mixed conduction effects, involving extended and localized 517 states. However, with the aim to confirm in our samples the 518 departure from the nearly piecewise linear behavior predicted 519 by Eq. (2) for the Arrhenius plot of the conductivity data, the 520 $\log_{10}[d\ln(\sigma)/d\ln(T)]$ function was numerically calculated 521 from the conductivity of our samples, following the approach 522 of, among others, Ref. 33. The slope *p* of the resulting data, 523

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plotted as a function of $log_{10}[T]$, is expected to equal the 524 value -1 when the conductivity exhibits a thermally activated 525 behavior, like $\sigma_0 e^{-\epsilon/K_BT}$. Similarly, the sum of two (or more) 526 thermally activated behaviors, as they are in Eq. (2), must 527 lead to two (or more) linear traits with slope p = -1. This is 528 sketched in the inset of Fig. 4(a), which plots in double loga-529 rithmic scale, the calculation of $d\ln(\sigma_{teo})/d\ln(T)$ performed 530 on a test function $\sigma_{teo} = \sigma_{01}e^{-\epsilon_1/K_BT} + \sigma_{03}e^{-\epsilon_3/K_BT}$. The ex-531 pectation of a p = -1 slope is qualitatively fulfilled for the 532 low temperature data of the $1.5 \times 10^{20} \text{ cm}^{-3}$ Al implanted 533 samples, as it appears in Fig. 4(a) for sample 305b of Table I, 534 535 for which the hypothesis of thermally activated hopping conduction between localized states at low temperature is con-536 537 firmed. At the same time, Fig. 4(a) shows that the higher 538 temperature conductivity data of sample 305b, which should correspond to valence band state transport, agree with a p 539 value a little higher than unity. This is consistent with non-540



FIG. 4. Plot of $\log_{10}[d\ln(\sigma)/d\ln(T)]$ versus $\log_{10}[T]$ for the measured σ of (a) sample 305b of Table I (Al = nted density of $1.5 \times 10^{20} \text{ cm}^{-3}$, CA 1950 °C/5 min; full square), (b) for sample 293e of Table I (Al implanted density of $3 \times 10^{20} \text{ cm}^{-3}$, CA 1950 °C/5 min; full triangle). Inset of Figure (a): $\log_{10}[d\ln(\sigma_{teo})/d\ln(T)]$ versus $\log_{10}[T]$ for the test function $\sigma_{teo} = 300 \exp(-0.1/K_BT) + 0.45 \exp(-0.021/K_BT)$, which roughly approximate the conductivity data of the sample of Figure (a) like the sum of two thermally activated contributions (see Eq. (2)). For guiding the eyes, straight lines with slope either -1 or -0.25, are also shown in the figures. Moreover, for reference, a vertical thin line is placed at about RT and the linear temperature scale is shown on the top axis, while arrows are drawn to point the transition region between two different transport regimes.

exact linearity of the high temperature data in the Arrhenius 541 plot of Fig. 3(b), due to the effective temperature dependence 542 of the total VB density of the states and of the carrier mobility. 543 A transition region exists between these two different trans- 544 port regimes, indicated by an arrow in Fig. 4(a), consistent 545 with the trend of the theoretical example reported in the inset 546 of the same figure. Fig. 4(b) reports the result of the same type 547 of analysis of Fig. 4(a) but for one of the 3×10^{20} cm⁻³ Al 548 implanted samples, more precisely sample 293e of Table I: 549 notwithstanding the scattering of the data; at low temperature, 550 their slope undoubtedly departs from the value p = -1, which, 551 however, seems to be a slope occurring just around RT. This 552 preliminary result roughly suggests the appearance of a trans- 553 port mechanism at lower temperatures different from the near- 554 est neighbor hopping, consistent with the Mott law 555 $\sigma = \sigma_0 e^{-\epsilon/K_B T^{0.25}}$. A nearest neighbor hopping transport, 556 instead, could not be excluded around RT. The Mott law has 557 been derived in the treatment of the variable range hopping, 558 which is a transport mechanism effectively expected in prox- 559 imity of the MIT transition,³¹ previously never pointed out in 560 p-type 4H-SiC. However, the given Mott law seems not to 561 fully explain the temperature $\boxed{}$ ndence of all the heaviest 562 doped samples here discussed, although for all them, the de- 563 parture of the conductivity from Eq. (2) is confirmed. 564

CONCLUSIONS

In conclusion, the unusual electrical prospective solution is $\geq 3 \times 10^{20} \text{ cm}^{-3}$ Al implanted 4H-SiC samples that allow us 567 to observe an IB conduction over a large temperature win-568 dow just arous. T associated to a low p-type 4H-SiC mate-569 rial resistivity is possible thanks to the simultaneous 570 occurrence of three aspects 571

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- (1) An implanted dopant concentration above the Al solubil- 572 ity limit of 2×10^{20} cm⁻². 573
- (2) A very efficient electrical activation process due to the 574 extremely high post implantation annealing temperatures 575 of 1950 °C and 2000 °C.
- (3) The high thermal ionization energy of the acceptors in p- 577 type 4H-SiC. 578

A nearly temperature independent free hole density 579 can be obtained around RT in these samples, a feature that 580 can guarantee good thermal stability in applications where 581 such a stability is required. Ion implantation even permits 582 to simplify the processing steps for reaching such a condi-583 tion in selected areas. Weakly T-dependent transport prop- 584 erties were obtained, in this work, at lower implant dose 585 and higher electrical activation of the implanted impurities 586 in respect to results of other authors. No significant effects 587 due to the implant temperature variation between 300 °C 588 and 400 °C were evidenced. In $5 \times 10^{20} \text{ cm}^{-3}$ Al implanted 589 samples, hole density values overcoming the Al solubility 590 limit in 4H-SiC were reached, consistent with at least a 591 50% electrical activation if a 15% compensation is sup- 592 posed. These doping conditions lead to the lowest RT resis- 593 tivity values ever reported in the literature for p-type 4H- 594 SiC, to the best of the authors knowledge, with more 595 favourable results in MWA samples, owing to the 50°C 596

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higher temperature of the treatment in respect to CA. The 597 temperature dependence of the resistivity was well 598 explained by the model of Miller and Abrahams in the 599 samples of carrier density lower than 3×10^{20} (here inves-600 tigated and from the literature), whereas a deviation from 601 this behaviour is observed above such a density, consistent 602 with the occurrence of a variable range hopping transport 603 mechanism at low temperatures. 604

Theory and experiments on impurity band conduction 605 606 lead to conclude that such a transport mechanism takes place at higher and higher temperature with the increasing of the 607 dopant ionization energy. SiC is certainly a good material to 608 see this trend because of the quite deep energy level of every 609 610 dopant species. Actually, SiC was the first semiconductor 611 where transport through an impurity band was hypothesized in 1946.³⁴ The novelty to see an impurity band transport 612 around room temperature in p-type SiC dates on the years 613 2004–2006, roughly.^{8,9,32} The novelty to obtain an impurity 614 band transport with features of interest for practical devices 615 is shown in the present study. 616

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- 630 ¹R. Nipoti, F. Moscatelli, and P. D. Nicola, IEEE Electron Device Lett. 34, 631 966 (2013).
- ²A. Nath, V. R. Mulpuri, Y.-L. Tian, A. Parisini, and R. Nipoti, J. Electron. 632 633 Mater. 43, 843 (2014).
- 634 ³A. Nath, A. Parisini, Y.-L. Tian, V. R. Mulpuri, and R. Nipoti, Mater. Sci. 635 Forum 778–780, 653 (2014).
- 636 ⁴R. Nipoti, R. Scaburri, A. Hallén, and A. Parisini, J. Mater. Res. 28, 17 637 (2013).

- J. Appl. Phys. 118, 000000 (2015)
- ⁵R. Nipoti, A. Hallén, A. Parisini, F. Moscatelli, and S. Vantaggio, Mater. 638 639 Sci. Forum 740-742, 767 (2013).
- ⁶M. K. Linnarsson, U. Zimmermann, J. Wong-Leung, A. Schöner, M. S. Janson, 640 C. Jagadish, and B. G. Svensson, Appl. Surf. Sci. 203-204, 427 (2003). 641
- ⁷R. Nipoti, A. Nath, M. V. Rao, A. Hallen, A. Carnera, and Y. L. Tian, 642 643 Appl. Phys. Express 4, 111301 (2011).
- ⁸V. Heera, K. N. Madhusoodanan, W. Skorupa, C. Dubois, and H. 644 645 Romanus, J. Appl. Phys. 99, 123716 (2006).
- ⁹Y. Negoro, T. Kimoto, H. Matsunami, F. Schmid, and G. Pensl, J. Appl. 646 647 Phys. 96, 4916 (2004). 648
- ¹⁰A. Parisini and R. Nipoti, J. Appl. Phys. **114**, 243703 (2013).
- ¹¹M. Laube, F. Schmid, G. Pensl, G. Wagner, M. Linnarsson, and M. Maier, 649 J. Appl. Phys. 92, 549 (2002). 650 651
- ¹²See http://www.srim.org/ for SRI ¹³Y.-L. Tian, MRS Bull. **35**, 181 (2010).
- ¹⁴H. M. Ayedh, V. Bobal, R. Nipoti, A. Hallen, and B. G. Svensson, J. Appl. 653 654 Phys. 115, 012005 (2014).
- ¹⁵R. Nipoti, F. Mancarella, F. Moscatelli, R. Rizzoli, S. Zampolli, and M. 655 656 Ferri, Electrochem. Solid-State Lett. 13, H432 (2010).
- ¹⁶S. G. Sundaresan, V. R. Mulpuri, Y.-L. Tian, M. C. Ridgway, J. A. 657 Schreifels, and J. J. Kopanski, J. Appl. Phys. 101, 73708 (2007). 658
- ¹⁷R. Chwang, B. J. Smith, and C. R. Crowell, Solid-State Electron. **17**, 1217 659 660 (1974).
- ¹⁸N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline* 661 Materials (Clarendon Press, Oxford, 1971), Chap. 2, p. 53; Chap. 6, p. 152. 662 ¹⁹F. Schmid, M. Krieger, M. Laube, G. Pensl, and G. Wagner, in Hall 663 Scattering Factor for Electron and Holes in SiC in Silicon Carbide, 664 665 Recent Major Advances, edited by W. J. Choyke, H. Matsunami, and G. 666 Pensl (Springer-Verlag, Berlin/Heidelberg, 2004), p. 517.
- ²⁰J. D. Wiley, in *Mobility of Holes in III-V Compounds*, Semiconductor and 667 668 Semimetals, edited by R. K. Willardson and A. C. Beer (Academic Press, New York, 1975), Vol. 10, p. 91. 669 670
- ²¹A. Koizumi, J. Suda, and T. Kimoto, J. Appl. Phys. **106**, 013716 (2009). 671
- ²²J. Pernot, S. Contreras, and J. Camassel, J. Appl. Phys. **98**, 023706 (2005).
- ²³T. Holstein, Phys. Rev. **124**, 1329 (1961).
- ²⁴D. Emin, Philos. Mag. 35, 1189 (1977).
- ²⁵A. Chandra, C. E. C. Woodard, and L. F. Eastman, Solid State Electron. 674 22, 645 (1979). 675
- ²⁶P. Achatz, J. Pernot, C. Marcenat, J. Kacmarcik, G. Ferro, and E. 676 Bustarret, Appl. Phys. Lett. 92, 072103/1-3 (2008). 677 678
- ²⁷V. Heera, D. Panknin, and W. Skorupa, Appl. Surf. Sci. **184**, 307 (2001).
- ²⁸A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).
- ²⁹E. A. Davis and W. D. Compton, Phys. Rev. 140, A2183 (1965).
- ³⁰H. Fritzsche and M. Cuevas, Phys. Rev. **119**, 1238 (1960).
- ³¹B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped* 682 Semiconductors (Springer-Verlag, Berlin/Heidelberg, 1984), p. 74. 683 ³²R. Müller, U. Künecke, R. Weingärtner, M. Maier, and P. Wellmann, 684 685
- Phys. Status Solidi C 3, 554 (2006). ³³A. Y. Rogatchev and U. Mizutani, Phys. Re 1, 15550 (2000).
- ³⁴G. Busch and H. Labhart, Helv. Phys. Acta 14, 463 (1946).

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