

## Hydrogen passivation and reactivation of the Al-acceptors in p-type 6H-SiC

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 9011

(<http://iopscience.iop.org/0953-8984/13/40/317>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 14:56

Please note that [terms and conditions apply](#).

# Hydrogen passivation and reactivation of the Al-acceptors in p-type 6H–SiC

M E Samiji<sup>1</sup>, A Venter<sup>2</sup>, M C Wagener<sup>1</sup> and A W R Leitch<sup>1</sup>

<sup>1</sup> Department of Physics, University of Port Elizabeth. PO Box 1600, Port Elizabeth 6000 South Africa

<sup>2</sup> Department of Physics, Vista University, Private Bag X613, Port Elizabeth 6000 South Africa

E-mail: phbmes@upe.ac.za and vnter-a@pelican.vista.ac.za

Received 2 May 2001

Published 20 September 2001

Online at [stacks.iop.org/JPhysCM/13/9011](http://stacks.iop.org/JPhysCM/13/9011)

## Abstract

We report on the passivation by hydrogen and the subsequent thermal reactivation of the acceptors in Al-doped p-type 6H–SiC. Capacitance–voltage measurements revealed that the near-surface free carrier concentration was reduced by at least an order of magnitude after hydrogen plasma treatment. The thermal stability of the Al–H complex in hydrogenated SiC was investigated through a series of isothermal anneals at temperatures ranging from 200 to 275 °C, while applying a reverse bias to a Ru Schottky barrier. Ru was chosen as the Schottky barrier metal for both its permeability to hydrogen as well as its thermal stability. The electric field associated with the applied reverse bias caused the dissociated hydrogen to drift deeper into the material, thereby confirming the positive charge state of atomic H in p-type SiC. The thermal dissociation of the electrically neutral Al–H complex was found to obey first-order kinetics for temperatures above 225 °C with a dissociation energy of  $(1.51 \pm 0.12)$  eV.

## 1. Introduction

Hydrogen is known to readily passivate shallow acceptors in various semiconductors, including SiC [1], through the formation of electrically neutral acceptor–hydrogen complexes. Unintentional incorporation of hydrogen into SiC commonly occurs during chemical vapour deposition [2]. Intentional incorporation has also been achieved by heating in H<sub>2</sub> gas at high temperatures and pressures [3], as well as by ion implantation [4] and exposure to a hydrogen plasma [5]. Because of the primary role hydrogen plays during the growth and subsequent processing of devices, it is important that the interaction of hydrogen with the shallow acceptors in SiC be fully understood.

Most experimental and theoretical studies on hydrogen in SiC have been conducted on 4H-SiC [6]. In this paper we report the passivation and reactivation of the Al acceptors in p-type 6H-SiC.

## 2. Experimental details

Al-doped ( $p = 4 \times 10^{17} \text{ cm}^{-3}$ ) 6H-SiC material, obtained from Cree Research Inc, was used in this study. The material was cleaned in standard organic solvents and dipped in a dilute HF solution before being dried in a flow of  $\text{N}_2$  and loaded in the vacuum chamber. Low resistance ohmic contacts were formed by thermally evaporating Al (180 nm) and Ti (50 nm) on the back surfaces, after which the samples were annealed for 10 min at 600 °C, followed by a further 5 min at 900 °C. Schottky diodes (about 45 nm thick; 0.8 mm diameter) were formed by electron beam evaporation of ruthenium through a metal shadow mask onto the polished surface of the material. We have previously reported that Ru forms a thermally stable Schottky contact on p-type 6H-SiC, with a barrier height of 1.06 eV [5].

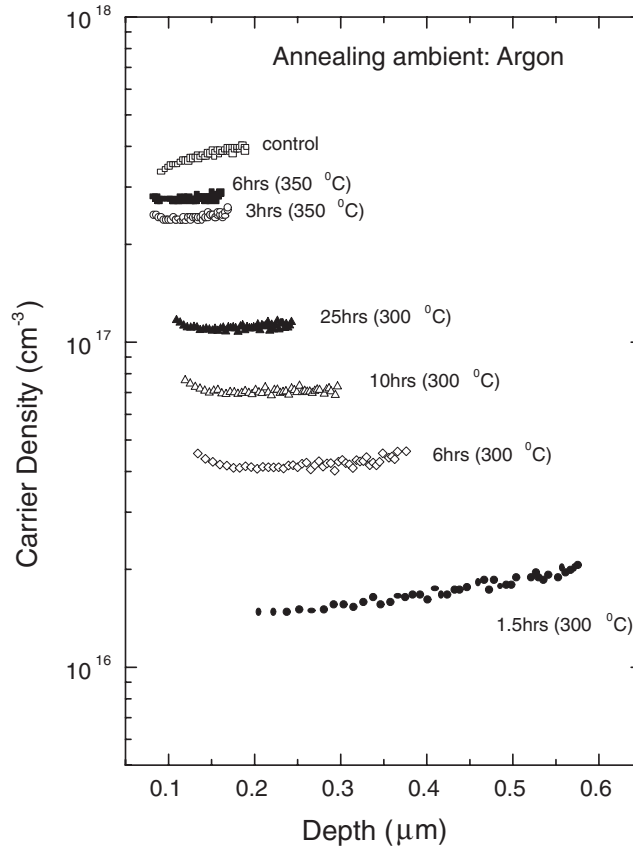
Hydrogen was introduced into the SiC by exposing the Schottky diodes for 30 min to a dc hydrogen plasma (having a plate voltage of 600 V). This alternative approach of hydrogenating the material through the Ru contacts, instead of exposing the SiC surface directly to the plasma, has several advantages: firstly, the metal film reduces near-surface damage that could impede the reactivation of the Al-H complexes, and secondly, the built-in field of the Schottky diode reduces the accumulation of near-surface hydrogen by causing field-assisted drift of positively charged hydrogen species away from the surface during hydrogenation. The samples were placed on a heater block 10 cm downstream from the plasma, and were biased to  $-100 \text{ V}$  relative to the plasma. The hydrogen pressure was 0.5 mbar and the sample temperature was held at 200 °C. Note that this temperature is lower than what is generally used for the introduction of hydrogen into SiC [7].

Standard capacitance-voltage ( $C-V$ ) measurements at 1 MHz were used to profile the hole concentration at room temperature, while current-voltage ( $I-V$ ) measurements enabled one to monitor the quality of the Schottky diodes before and after each annealing experiment. To investigate the thermal stability of the Al-H complex formed during the hydrogen plasma treatment, a series of anneals was performed in air in the dark with the samples placed in a quartz furnace tube. Reverse bias annealing (RBA) experiments were carried out at temperatures ranging from 200 to 295 °C, with a reverse bias applied to the Schottky diode. The temperature was monitored by a thermocouple mounted next to the SiC sample. After each annealing step the sample was rapidly cooled to room temperature by pouring liquid nitrogen onto the sample holder while still maintaining the reverse bias.

## 3. Results and discussions

Subjecting the Schottky diode to the hydrogen plasma conditions described above was found to reduce the carrier concentration in the near-surface region by more than an order of magnitude. Figure 1 shows the active acceptor concentration profiles after a series of anneals at 300 to 350 °C, *without* a reverse bias applied to the sample. Although there is a systematic increase in the active Al concentration, annealing the sample at 300 °C for 25 h only succeeded in partially reactivating the passivated Al acceptors. By comparison, annealing the sample *with* an applied reverse bias dramatically increased the reactivation process. This is illustrated in figure 2, which shows a series of isothermal anneals at 275 °C for increasing times, with a reverse bias of 5 V applied to the Schottky diode. In the region  $x < 0.175 \mu\text{m}$  of the space-charge

region, the Al acceptors become progressively more reactivated, while deeper in the material ( $0.175 \mu\text{m} < x < 0.5 \mu\text{m}$ ) a simultaneous deactivation of the Al acceptors takes place.



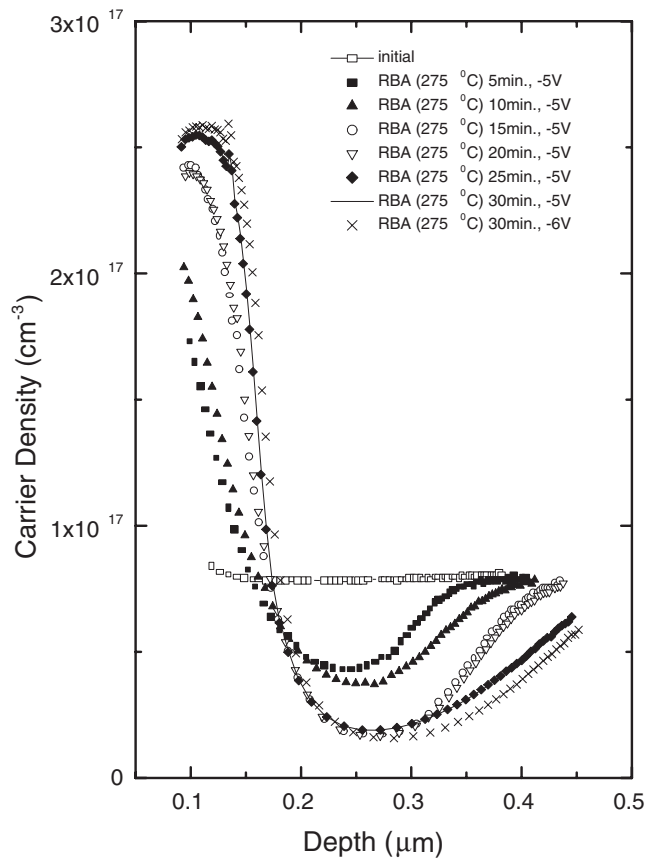
**Figure 1.** C-V depth profiles of the control (non-passivated) and hydrogen passivated p-type 6H-SiC.

The result shown in figure 2 is similar to what has recently been reported for Al-doped 4H-SiC [8] and what is known for acceptors in other semiconductors such as Si [9] and GaAs [10], and may be explained as follows. The hydrogen plasma treatment causes the formation of electrically neutral Al-H complexes, thereby reducing the free carrier concentration. Annealing the sample at elevated temperatures causes the thermal dissociation of the Al-H complex, according to the equation  $(\text{AlH})^0 \leftrightarrow \text{Al}^- + \text{H}^+$ . The released hydrogen is positively charged and will therefore undergo field-assisted drift deeper into the material, where it will recombine to form new Al-H complexes, thus reducing the carrier concentration in the region  $0.175 \mu\text{m} < x < 0.5 \mu\text{m}$ . The above reaction will therefore proceed predominantly towards the right in the high-field region of the Schottky diode.

The concentration profiles in figure 2 may therefore be considered to represent the electrically active Al concentration, provided the room-temperature concentration of  $\text{H}^+$  is negligible. The rate of formation and dissociation of the Al-H complex is described by

$$\frac{\partial[\text{AlH}]}{\partial t} = \sigma_{\text{AlH}}(p - [\text{AlH}][\text{H}^+] - \nu_{\text{AlH}}[\text{AlH}]) \quad (1)$$

where  $\sigma_{\text{AlH}}$  is the capture rate of  $\text{H}^+$  by  $\text{Al}^-$  and  $\nu_{\text{AlH}}$  is the dissociation frequency of the

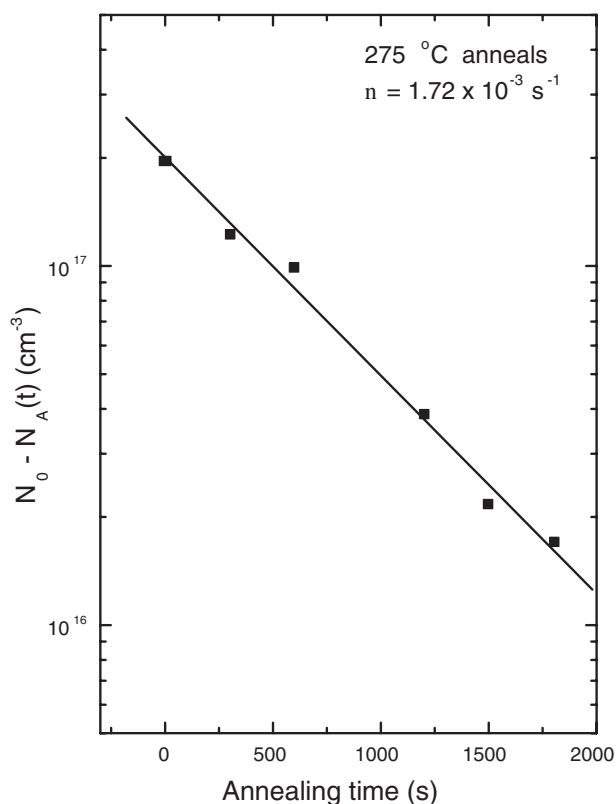


**Figure 2.**  $C$ - $V$  depth profiles of the active Al concentration as a function of reverse-bias annealing time, in hydrogen passivated p-type 6H-SiC.

Al-H complexes.  $[H^+]$  and  $[AlH]$  denote the concentration of free atomic hydrogen and Al-H complexes, respectively. If the electric field resulting from the reverse-biased Schottky diode is sufficiently high to suppress the recapture of hydrogen within the space-charge region, then the term  $v_{AlH}[AlH]$  will dominate the right-hand side of equation (1), resulting in a predicted first-order dissociation of the Al-H complex.

In order to quantitatively analyse the reactivation of the Al-H complexes in the high-field region of figure 2, the inactive Al concentration  $I(t) = N_0 - N_A(t)$  is measured at  $x = 0.1 \mu\text{m}$ , where  $N_0$  is the concentration in the unpassivated (control) sample and  $N_A(t)$  is the measured carrier concentration after an annealing time  $t$ . The linear fit shown in figure 3 confirms the first-order reactivation of the Al-H complexes and may be described by the expression  $I(t) = I_{(t=0)} \exp[-v_{AlH}(T)t]$ , with  $v_{AlH}(275^\circ\text{C}) = 1.72 \times 10^{-3} \text{ s}^{-1}$ .

It was found that the reactivation kinetics deviated from first-order after long anneal times. This was particularly the case for anneals at  $200^\circ\text{C}$  (the lowest temperature investigated). Zundel and Weber previously reported such an effect for hydrogen passivated B-doped Si [9]. They attributed the deviation from first-order kinetics to the build up of hydrogen at the edge of the space-charge region. The saturation of available acceptor trapping centres then impedes the drift of hydrogen away from the high-field region. The resulting increase in  $[H^+]$ , together with the increased availability of electrically active acceptors within the space-charge region,

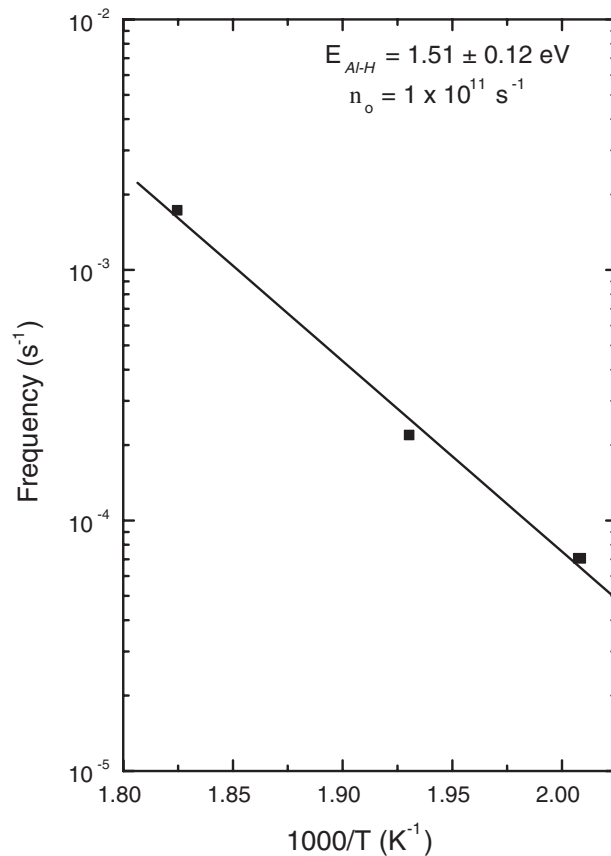


**Figure 3.** Inactive Al concentration versus anneal time, measured in the high-field region of a reverse-biased Schottky diode, the depth profiles of which are depicted in figure 2.

consequently causes the capture term in equation (1) to become significant.

The RBA experiments were repeated for other temperatures. The Arrhenius plot of the measured dissociation frequencies  $\nu_{AlH}(T)$  is shown in figure 4. The values satisfy the equation  $\nu_{AlH}(T) = \nu_0 \exp(-E_{AlH}/kT)$ , with a dissociation energy  $E_{AlH}$  of  $(1.51 \pm 0.12)$  eV and an attempt frequency  $\nu_0 = 1 \times 10^{11} \text{ s}^{-1}$ . This dissociation energy is slightly lower than the value of 1.66 eV measured by Janson *et al* [11] who used an effective diffusion constant method to determine the dissociation energy for the  $^2\text{H}$ -Al complex in 4H-SiC. It is however significantly higher than the value of 1.2 eV obtained by Hülßen *et al* [8] for  $^1\text{H}$ -Al in similar 4H-SiC. The latter value was obtained from a simulation in which the dissociation of the Al-H complex is considered as four independent steps [8]. The quoted value of 1.2 eV is associated with the dissociation of the Al-H complex *alone* and does not consider the energy required for diffusion beyond the capture radius of the acceptor. In both studies [8, 11], hydrogen was introduced into the material by means of ion implantation. It is well known that ion implantation results in damage that may impede the reactivation of the Al-H complex and therefore the validity of the measured dissociation energy. In a similar experiment, Hülßen *et al* [12] previously reported an upper limit for the dissociation energy of 1.8 eV in epitaxially grown p-type 4H-SiC. They however did not report an attempt frequency for the dissociation process. One would expect the attempt frequency  $\nu_0$  to be of the same order as the lattice-phonon vibration frequencies ( $\sim 10^{13} \text{ s}^{-1}$ ). The fact that the present value of  $1 \times 10^{11} \text{ s}^{-1}$  is almost two orders of magnitude lower, may be related to the fact that the small error in the dissociation energy translates

to a large error (an order of magnitude) in the attempt frequency. It should also be noted that although care was taken to measure the sample temperature as accurately as possible, the error associated with carrying out reactivation experiments at elevated temperatures for predetermined time increments, became increasingly large. In fact, although we attempted anneals at 295 °C, the errors introduced were unacceptably large.



**Figure 4.** Arrhenius plot of the dissociation frequencies for the Al–H complex for the three different temperatures namely 225, 245 and 275 °C.

#### 4. Conclusions

We have shown that Al-doped p-type 6H–SiC can be passivated by hydrogen introduced using a dc hydrogen plasma system at temperatures as low as 200 °C. When applying a reverse bias, successful first-order reactivation of the passivated acceptors was achieved at temperatures of 225 °C and above. The observed drift towards the low-field region of the reverse-biased Schottky barrier diode also confirmed the positive charge state of hydrogen in 6H–SiC. Finally we measured a dissociation energy of  $(1.51 \pm 0.12)$  eV which we believe to be the first direct determination for the Al–H complex in 6H–SiC.

## Acknowledgments

This work was funded by the South African National Research Foundation, under the Hungary–South Africa Bilateral Agreement. We thank P Déak for fruitful discussions. MES gratefully acknowledges the financial support of the Third World Organization for Women in Sciences, Trieste, Italy.

## References

- [1] Pearton S J, Corbett J W and Stavola M 1992 *Hydrogen in Crystalline Semiconductors* (Berlin: Springer)
- [2] Larkin D J, Sridhara S G, Devaty R P and Choyke W J 1995 *J. Electron. Mater.* **24** 289
- [3] Gendron F, Porter L M, Porte C and Bringuier E 1995 *Appl. Phys. Lett.* **67** 1253
- [4] Achtziger N, Grillenberg J, Witthuhn W, Linnarsson M K, Janson M and Svensson B 1998 *Appl. Phys. Lett.* **73** 945
- [5] Samiji M E, van Wyk E, Wu L, Venter A and Leitch A W R 2001 *Mater. Sci. Forum* **353–356** 607
- [6] Aradi B, Gali A, Deák P, Lowther J E, Briddon P R, Son N T, Janzén E and Choyke W J 2000 *Phys. Rev. B* **63** at press
- [7] Ren F, Grow J M, Baskaran M, Wilson R G and Pearton S J 1997 *J. Electron. Mater.* **26** 198
- [8] Hülsen C, Achtziger N, Herold J and Witthuhn W 2001 *Mater. Sci. Forum* **353–356** 331
- [9] Zundel T and Weber J 1989 *Phys. Rev. B* **39** 13 549
- [10] Wagener M C, Botha J R and Leitch A W R 2000 *Phys. Rev. B* **62** 15 315
- [11] Janson M S, Hallén A, Linnarsson M K, Nordell N, Karlsson S and Svensson B G 2001 *Mater. Sci. Forum* **353–356** 427
- [12] Hülsen C, Achtziger N, Reislöhner U and Witthuhn W 2000 *Mater. Sci. Forum* **338–342** 929