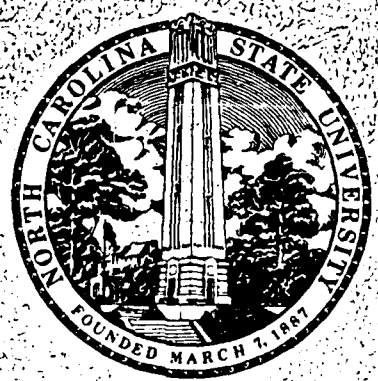


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Annual Letter Report
 on
**Fundamental Studies and Device Development
 in Beta Silicon Carbide**
Supported by ONR Under Contract N00014-82-K-0182 P0009
 For the Period February 1, 1988 — January 31, 1989



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<p>Studies in this time period have been concerned with the doping of 6H-alpha SiC with Al and the development of fabrication schemes for several high frequency and high power device structures. The atomic concentration and the p-type carrier concentration have been determined. The former has a maximum of approximately 2×10^{21}. The carrier concentration is approximately 500 times less than the atomic concentration at all concentration levels. A variety of devices and fabrication schemes have been designed including those for MESFETs, IMPATT diodes, Shockley diodes and heterostructure bipolar transistors. Research concerned with making these devices is now ongoing.</p>			
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I. Introduction

Silicon carbide is the only compound species that exists in the solid state in the Si-C system, but it can occur in many polytype structures. The lone cubic polytype crystallizes in the zinc blende structure and is denoted as β -SiC. The ~170 known additional hexagonal and rhombohedral polytypes are collectively referred to as α -SiC. The electron Hall mobility of high-purity undoped β -SiC has been postulated from theoretical calculations to be greater than that of the α forms over the temperature range of 300–1000K because of the smaller amount of phonon scattering in the cubic material. Although this result has served as one catalyst for the current international interest in β -SiC, this material also possesses a unique combination of additional properties including a high melting point (3103K at 30 atm), high thermal conductivity (3.9 W/cm·deg), wide bandgap (2.2 eV at 300 K) and high breakdown electric field (2.5×10^6 V/cm). As such, β -SiC has been theoretically shown to be superior to Si, GaAs or InP using either Johnson's or Keyes' figure of merit for high-frequency, high-speed and high-power transistor applications.

The high thermal conductivity and breakdown field also indicate that the integration of devices made from β -SiC can be achieved with high densities. Two additional reasons for the renewed interest in β -SiC are the significant advances in the growth of monocrystalline thin films of this material by chemical vapor deposition (CVD) and the ability to dope this material with n- and p-type dopants growth or via ion implantation. As a result, devices from this material have now become a reality.

In this reporting period, we have concentrated on studies concerned with the doping of Al in 6H SiC and the development of fabrication schemes for several high-frequency and high-power device structures. Where necessary, the masks for these devices have been ordered or received and fabrication is ongoing on several fronts. Experimental directions and results of this research are described below.



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II. Aluminum Incorporation into 6H SiC Films

A. Introduction

The best choice of substrates for the growth of SiC films is SiC single crystals. Silicon carbide has been epitaxially grown on α -SiC substrates since the late 1960's. Several investigators have reported on the growth of α -SiC on α -SiC substrates in the temperature ranges 1773–2023K [1–3] and 1593–1663K [4] with growth directions parallel and perpendicular respectively to the [0001] axis. The growth of β -SiC on α -SiC substrates in the temperature range of 1773–1973K [5,6] and the growth of β -SiC on β -SiC substrates in the temperature range of 1473–2073K [7] have also been studied.

The use of 6H-SiC {0001} substrates for the growth of β -SiC films in our laboratory resulted in a substantial reduction in the defect density at the film/substrate interface [8]. High quality 6H-SiC films grown on off-axis 6H α -SiC substrates have also been grown in our laboratory by Kong *et al* [9]. Such films are very suitable for device fabrication. It is also important that we understand the process technology for doping these material with p-type dopants. Among the choice of dopants, Al has become the recognized standard at this time. This section of the report presents the results of theoretical and empirical studies of Al incorporation into 6H-SiC films during epitaxial growth via in situ chemical vapor deposition (CVD) doping. (A companion study regarding the incorporation of n-type dopants in 6H-SiC is currently under investigation.)

B. Theoretical Considerations

Dopant species are presumed to follow Henry's law when introduced, but not electrically activated (ionized), into SiC. This statement is based on the equilibrium solubility model of Rai-Choudhury and Salkovitz [10] which incorporates dilute solution thermodynamics. The solute atoms are considered to exist in monoatomic form. The overall reaction to the dopant species entering into the solution in the SiC is

$$D_y(g) = yD \text{ (in the SiC crystal)} \quad [1]$$

where D_y is the dopant gas species, y is the number of dopant atoms per molecule of the dopant gas species and D is the single dopant atom in the SiC crystal.

The equilibrium constant of the reaction may be expressed as

$$K = \frac{\alpha_D^y}{P_{Dy}} = \frac{v_D^y N_D^y}{P_{Dy}} \quad [2]$$

where α_D is the activity of the dopant species, P_{Dy} is the partial pressure of the dopant species, v_D^y is a proportionality constant (it is the activity coefficient if N_D is the mole fraction of dopant species), and N_D is the concentration of dopant in the SiC crystal.

Since we assume that Henry's law is followed, at constant temperature,

$$N_D = \frac{K^{1/y}}{\delta_D} P_{Dy}^{1/y} = K' P_{Dy}^{1/y} \quad [3]$$

where K' is a new proportionality constant. By taking the logarithm of both sides of Eq. 3, one obtains

$$\log N_D = \log K' + (1/y) \log P_{Dy} \quad [4]$$

The ratio of the ionized dopant concentration to the total dopant concentration in the SiC crystal may be defined as follows

$$\gamma_D = \frac{N_i}{N_D} \quad [5]$$

where N_i is the ionized dopant concentration at some actual N_D . Combining Eq. 3 and 5, one obtains

$$N_i = K' \gamma_D' (P_{Dy})^{1/y} \quad [6]$$

By taking the logarithm of both sides of Eq. 6, it becomes

$$\log N_i = \log (K' \gamma_D') + (1/y) \log P_{Dy} \quad [7]$$

Assuming that K' and γ are independent of the partial pressure of the given dopant species, Eqs. 4 and 7 predict that plots of $\log N_D$ vs. P_D and $\log N_i$ vs. $\log P_D$ should be linear and parallel with a slope of $1/y$ within the range of values of N_D where Henry's law is valid.

To obtain a value of $1/y$ for the Al dopant, it is necessary to experimentally this dopant at several known partial pressures into the growth chamber during deposition and to subsequently measure its atomic and carrier concentrations in the resultant α -SiC films.

C. Experimental Procedures

In this research, black, industrial 6H-SiC crystals obtained from an Acheson furnace were employed as the substrates for the in situ CVD doping of 6H-SiC. The substrates were lapped 3° off [000T] towards [11 $\bar{2}$ 0] orientation and polished down to 0.1 μm diamond paste. Each 6H-SiC substrate was then oxidized at 1473K in a flowing dry oxygen atmosphere to remove an approximately 50 nm subsurface damage caused by the mechanical polishing. The oxide layer on each substrate was removed with a HF acid solution immediately prior to loading on a SiC-coated graphite susceptor which held the samples during growth. A cold wall, vertical barrel-type, rf-heated system which was evacuated to 10^{-6} Torr before growth to remove air and moisture was used for the deposition (see Ref. 22 for the system detail).

Al dopant gas was incorporated directly into the primary gas stream containing C_2H_4 , SiH_4 and H_2 for the chemical vapor deposition of 6H-SiC under the growth condition of 1723K and 1 atm total pressure. The flow rates of C_2H_4 , SiH_4 and H_2 were 1, 2, and 3000 sccm, respectively. Liquid trimethylaluminum ($\text{Al}(\text{C}_2\text{H}_5)_3$) (TMA) was used as the source of Al. The concentration of TMA in the gas stream was altered both by changing the flow rate of H_2 over the TMA and by changing the temperature of the bath containing the bottle of TMA (temperature controlled with $\pm 0.1\text{K}$). The vapor pressure of TMA at a specific temperature was calculated by using the equation:

$$\log P_V = 7.3147 - \left(\frac{1534.1}{T-53} \right) \quad (8)$$

where P_V is the vapor pressure of TMA in mmHg and T is the temperature in degree Kelvin. Eq. 8 is effective in the temperature range of 290–373K. The number of moles of TMA carried into the reaction chamber by H_2 per unit time as a result of its flow through the TMA bottle was calculated by using the ideal gas equation

$$n = \frac{PV}{RT}$$

where n is the number of moles of TMA introduced into the reaction chamber per unit time, P is the vapor pressure of TMA obtained from Eq. 8, V is the volume occupied by TMA per unit time, which was obtained from the flow rate of H_2 from the TMA, T is the temperature of the bath containing the bottle of TMA and R is the gas constant.

The amounts of introduction of Al into the epitaxial 6H-SiC films have been analyzed quantitatively as a function of depth using secondary ion mass spectrometry (SIMS). Oxygen was used as the primary ion with a beam size of 250 μm . The atomic concentration

of Al at each point in the SIMS profile was obtained by multiplying a conversion factor by the value of the Al/Si count ratio at this point. The conversion factor was determined from the product of the Al/Si count ratio and the theoretically calculated atomic concentration at the peak of an Al implanted profile standard.

The amounts of ionized Al (carrier concentration) in the epitaxial 6H-SiC films were determined by the differential capacitance-voltage technique. In this method, the capacitance of the 6H-SiC film was measured as a function of a reverse voltage by using a 590 CV analyzer with a Hg-probe which produced both Ohmic and Schottky-barrier contacts on the surface of the epitaxial layer. The carrier concentrations of the layers were then calculated from the differential capacitance-voltage relationship.

D. Results

Figure 1 shows the results of the SIMS and CV measurements for the Al atomic and carrier concentrations as functions of the partial pressure of TMA. The linear and parallel characters of both the curves are predicted by Eq. 4 and 7. The slope ($1/y$) in the atomic concentration curve is 0.92 with a correlation coefficient of 0.98. The slope of ~ 1 indicates that the Al is in dilute solution in the 6H-SiC films and that pure Al and/or a complex containing only one Al atom are the principal species which contribute to the introduction of this dopant. The ratio of the carrier concentration to the atomic concentration is 0.02 at all partial pressures of TMA employed.

IV. Growth of p-n Structures for MESFETs

For the purpose of MESFET fabrication, a p-type layer with low carrier concentration is required for better insulation. The growth procedure and conditions of such p-type layers were the same as that described above, except that the TMA was kept in a constant temperature bath at around 291K and a low flow rate of H_2 over the TMA was used to produce a low doping level in the films.

After the growth of an approximately 2–3 μm thick p-type 6H-SiC layer the samples were then polished with 0.1 μm diamond paste to remove the surface roughness and oxidized at 1473K in flowing dry oxygen for 5400 s to remove approximately 50 nm of subsurface damage caused by polishing. The resulting oxide layer was removed in HF. These samples were reloaded on the SiC coated graphite susceptor for the growth of the n-type 6H-SiC layer.

Since unintentionally doped 6H-SiC shows n-type conductivity, no additional n-type dopants were introduced into the main gas stream during growth. The samples were heated to 1773K and remained at this temperature for 300 s to thermally etch the surfaces. The reactant gases of SiH₄ and C₂H₄ were subsequently introduced into the growth chamber. The thickness of the n-type layers are approximately 0.5 μm. The carrier concentrations in the n-type layers average about 5 × 10¹⁶/cm³. The hole concentrations in the p-type layers are in the range of 3–8 × 10¹⁶/cm³. The pinch-off voltage of such p-n structure, if the equilibrium contact voltage is negligible compared with gate-drain voltage, is about 11 V, calculated by using the following equation

$$V_p = \frac{\delta d^2 N_d}{2\epsilon}$$

where V_p is the pinch-off voltage, d is the thickness of the n-type layer, N_d is the donor concentration in the n layer, δ is the electronic charge and ϵ is the dielectric constant. The fabrication of MESFETs is now ongoing in this laboratory. Figure 2 shows a schematic structure of the MESFETs.

V. Device Designs and Fabrication Schemes

In addition to the MESFET structure described above and shown in Figure 2, designs and fabrication schemes have also been developed for IMPATT diodes, new MOSFET structures, heterojunction bipolar transistors and Shockley diodes. Where necessary, masks have been ordered and ground work research necessary to accomplish certain steps in the fabrication scheme are now being pursued and tested and the resulting materials examined for characteristics pertinent to the particular device. Details of the structure and fabrication schemes will be presented in subsequent reports.

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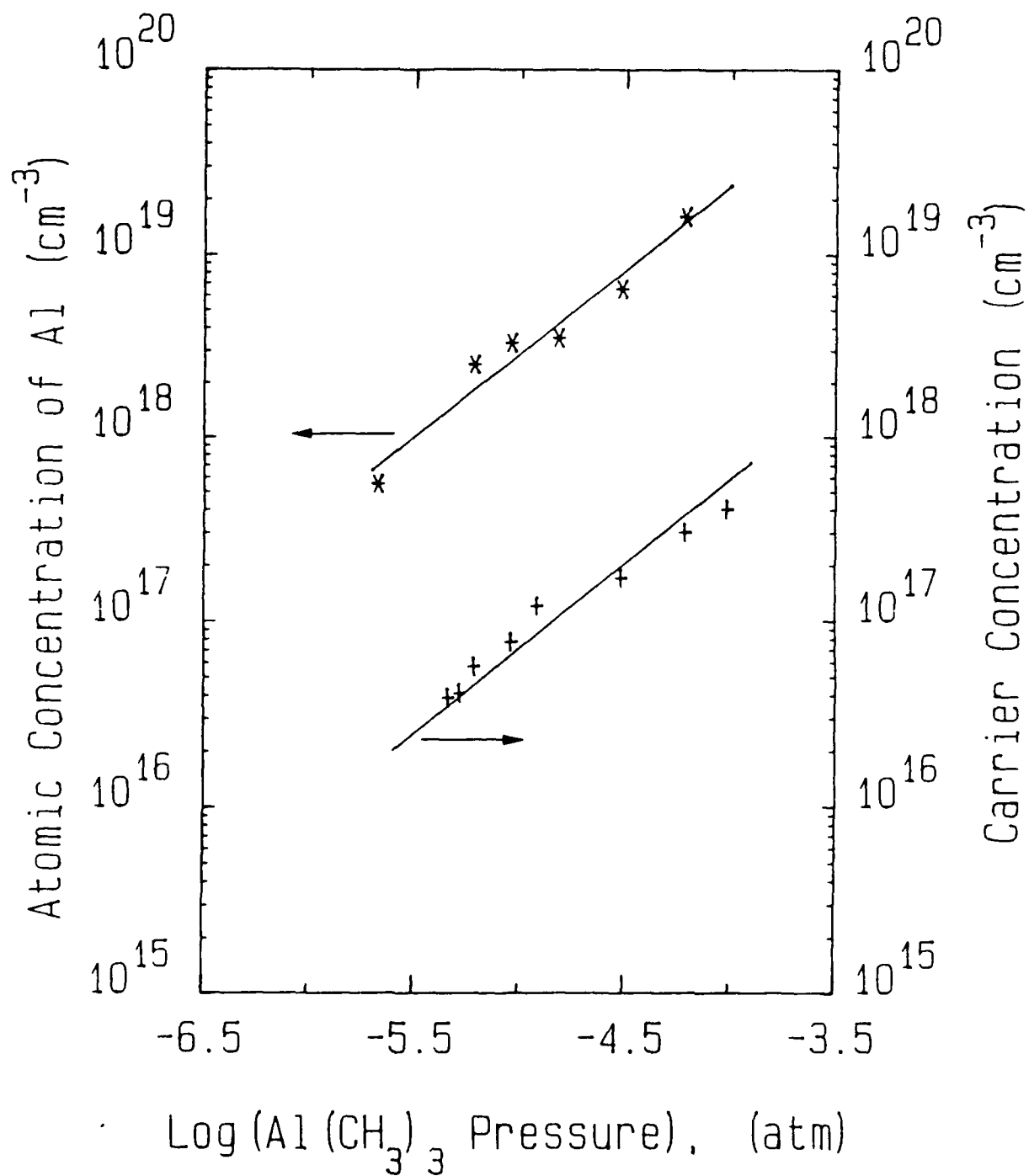


Figure 1. Atomic concentration of Al and the p-type carrier concentration of the doped 6H-SiC films as a function of the partial pressure of the dopant gas of $\text{Al}(\text{CH}_3)_3$ in the CVD chamber.

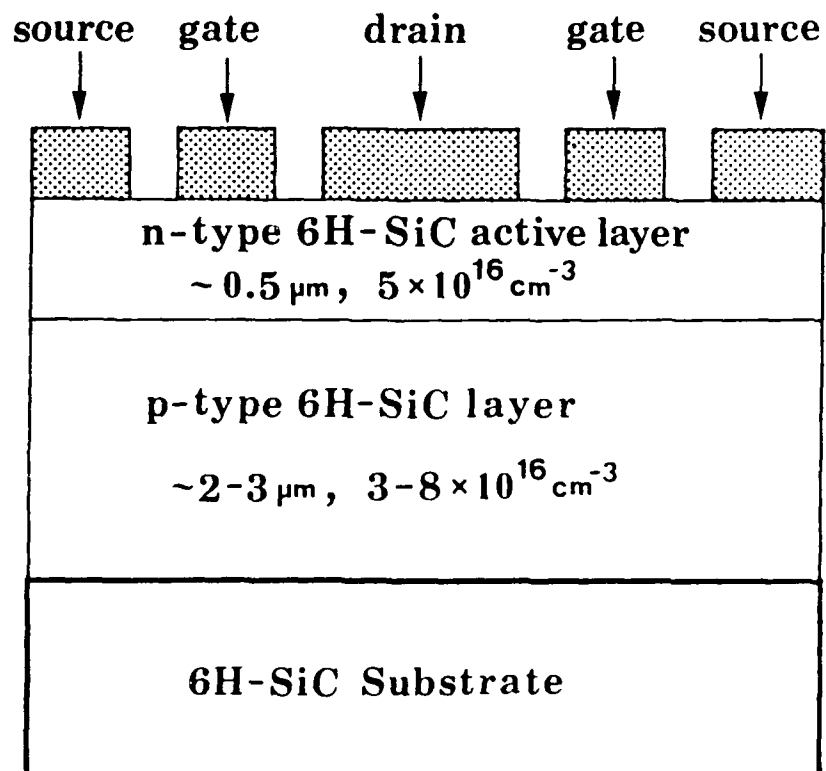


Figure 2. Schematic of the cross-sectional structure of the MESFET to be built at NCSU.

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