Obtaining SiC single crystals, and comparing characteristics of its solid solutions, films, Schottky diodes

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Abstract. The main methods for producing 4H-SiC single crystals and films of its solid solutions are considered. A new technique for producing single crystals of SiC polytypes is described. A new nonlinear model of the Schottky barrier height (BS) has been developed, and the current-voltage characteristics of Schottky diodes have been obtained, their comparison with the I–V characteristics of silicon-based diodes has been made.

1. Introduction

According to the conclusion of CREE [1–9], silicon carbide is the promising primary material for power electronics. We note a number of the most well-known technologies for producing SiC single crystals.

(a) Previously, direct ohmic heating technology was used to produce SiC. In this case, a SiC single crystal is grown from the gas phase in a growth chamber (crucible), where a field of operating temperatures of the order of 2500 °C is created [7].

(b) SiC sublimation technologies are also applied, where the temperature of the single seed crystal is kept below the temperature of the source [10–13].

(c) The technology for growing SiC single crystals using special thermal insulation is also of interest [14].

The main disadvantage of the above technologies is the lack of reliable control over the values of the working temperature gradients. The lack of reliable control leads to the appearance of a large number of cracks and impurities in the single crystal.

This article discusses a device that allows for the production of 4H-SiC polytypes by the method of controlled induction heating [9, 10]. In the device under consideration, additional oscillatory heating circuits are introduced for precise control of temperature field gradients.
The structure of the device for producing perfect silicon carbide single crystals is shown in Figure 1.

Figure 1. Scheme of a device for producing perfect single crystals of silicon carbide (SiC) using high-temperature induction heating (1 – source with a mixture of silicon carbide; 2 – the body of the growth chamber (crucible); 3 – inductor (induction coil); 4 – additional oscillatory circuit; 5 – seed single crystal)

An additional oscillating circuit (4) allows maintaining the necessary temperature gradients with high accuracy due to trim capacitors, providing a resonant mode with the inductor (3) – primary oscillatory circuit. The stability of the sublimation mode is maintained by changing the parameters of additional controlled oscillatory circuits.

In the growth zone, stable working temperature fields are created with an axial gradient in the direction from the seed crystal (5) to the source of silicon carbide (1). A stable field of operating temperatures ensures uniform evaporation of the source of silicon carbide and its crystallization from the vapor phase on the growth surface of the seed crystal. Uniform crystal growth is achieved by sublimation of SiC vapor from the gas phase in the growth chamber of the crucible by maintaining stable temperature gradients in the growth chamber and constant temperature values near the surface of the seed crystal. The crucible (2) of the proposed device contains housing and a lid with a pedestal, on which the SiC seed is fixed. At the base of the crucible, the body is a source of SiC (1) in the form of “pure” polycrystals or silicon carbide powder.

2. Theoretical part
2.1. Modified Schottky barrier height model for metal-semiconductor structures

It is known that in the contact region of structures, there are localized states of defects. In this situation, we consider the Schottky barrier height model [19, 21], but in a second-order approximation nonlinear in the concentration of defects. \( N_i = c \cdot 10^{13} \text{ cm}^{-2}\text{eV}^{-1} \), \( c = 0–30 \), where \( c \) is a convenient “concentration factor” in units of \( 10^{13} \text{ cm}^{-2}\text{eV}^{-1} \).

In this approach, along with the concentration of \( N_i \) defects, it is convenient to introduce the occupation numbers \( n_x(c) \). These numbers are determined by the form of the Hamiltonian of the system. In this approach, we obtain higher values of the Schottky barrier, which for small \( N_i \) \( (N_i<10^{13} \text{ cm}^{-2}\text{eV}^{-1} ) \) leads to better agreement with the experimental data than in the classical Bardin – Schottky – Mott model. In the model under consideration, the barrier height \( \Phi_B(c) \) is described by the formula [19, 21]:

\[
\Phi_B(c) = \Phi_m - \chi + \Delta \Phi_x(c)
\]  \( (1) \)
\[ \Delta \Phi_x (c) = 4\pi \left( e^2 / 4\pi \varepsilon_0 \varepsilon \right) \lambda N_x n_x (c) \]  

where \( \chi \) – the electron affinity; \( \Phi_m \) – the work function of the metal; \( \Delta \Phi_x (c) \) – the potential barrier due to the tunneling of carriers (electrons) between localized quasilevels \( (E_i) \) states and the metal; \( \lambda \) – the thickness of the contact region with permittivity \( \varepsilon \); \( N_x \) – surface density of localized states of defects, \( n_x (c) \) – the filling number of the quasilevel of the defect \( E_i \) with half-width \( \Gamma = \pi \rho U^2 \) \( (U \) is the hybridization energy of localized states and metal); \( \rho \) – the (constant) density of states of the metal; \( E_F \) is the Fermi level energy.

In this case, the metal in contact with the semiconductor is described by defective surface states \( |d> \) located in the forbidden zone. The metal in connection with the level \( |d> \), can be described by the Andersen’s Hamiltonian. In the simplest case, it has the following form [19]:

\[ H = \sum_c \varepsilon_c c^*_c c_c + E_i d^*_i d_i + U \sum_k (c^*_k d_k + h.c.). \]  

where \( \varepsilon_k \) – the electron energy; \( U \) – value of the matrix element of hybridization of the metallic \( |k> \) bond and the defective \( |d> \) state; \( c^*_k \) – the operator of the electron production with momentum \( |k> \); \( d^*_i \) – the electron creation operator in \( |d> \). If we assume that the Gaussian defective state \( E_i \) overlaps with a wide metal conduction band, i.e., in the range \( |E_0 - E| \leq \Gamma = \pi \rho U_0^2 \) \( (E_0 = E_i - E_F) \). Then one can find the state occupation numbers by the formula \( n_d = n_d (c) \):

\[ n_d (c) = \int_{-\infty}^{E_i} \rho_c (E) dE, \]  

\[ \rho_c (E) = \frac{1}{\pi} \frac{\Gamma}{(E - E_i)^2 + \Gamma^2}, \]  

\[ n_d (c) = \frac{1}{\pi} \int_{-\infty}^{E_i} \frac{\Gamma dE}{(E - E_i)^2 + \Gamma^2} = \frac{1}{\pi} \arccos \left( \frac{E_i - E_F}{\Gamma} \right). \]  

The forbidden zone of a semiconductor in a solid solution of silicon has the form

\[ E_x^i = E_x^i - ax + bx^2, \]  

where \( E_x = 3.3 \text{ eV}, \ a = 0.56, \ b = 3.86. \)

Then the position of \( E_F \) relative to the ceiling of the valence band is determined by the expression:

\[ E_x = \chi + E_x^i - \Phi_m - \Delta \Phi_x (c). \]  

Next, we introduce the notation

\[ (E_i - E_F) / \Gamma = \delta_i (c) \]  

\[ E_i = E_x^i \xi_i \]  

Moreover, for the state, \( \xi_i = 0.3 \) \( (0.5; 0.7) \), taking into account (9), we obtain:

\[ \Gamma \delta_i (c) = (\Phi_m - \chi) - (1 - \xi_i) E_x^i + \Delta \Phi_x (c) \]  

For the characteristic barrier width \( \lambda = 3\eta \hat{\lambda} \) \( (\eta = 0.5 - 2.0) \), the potential barrier \( \Delta \Phi_x \) has the form:

\[ \Delta \Phi_x (c) = k \eta \pi 2n_x (c) \]  

where the coefficient \( k = 0.272 \text{ eV} \). For justified values of \( E_F = E_x^i / 2 \), for \( E_F = E_x^i \) \( (\Gamma = 0.5 - 2.0 \text{ eV}) \), the quantity \( 2n_x (c) \approx 1 \). This data is in accordance with calculations in and gives the best agreement with the experimental data for the quantity \( \Phi^* y (c) \).
The Schottky barrier model nonlinear in the concentration of surface states is presented in [12, 21]. The approach given in [12, 21] shows higher values of the Schottky barrier. For low $N_i$ defect concentrations in the contact region ($N_i<10^{13} \text{ cm}^{-2} \cdot \text{eV}^{-1}$; $N_i=10^{13} \text{ cm}^{-2} \cdot \text{eV}^{-1}$), this leads to better agreement with the experimental data presented in [12, 13] than the formula Bardina, Schottky-Mott. Moreover, in our model, for the height of the potential Schottky barrier $\Phi_{bh}$ and the occupation numbers $n_i(c)$, we obtain [12, 13, 21]:

$$\Phi_{bh}(c) = p + k \eta 2\pi n_i(c).$$  \hspace{1cm} (13)

$$d_x(c) = p - (1 - \xi_i)E_g + k \eta \phi(1 - e V).$$  \hspace{1cm} (14)

$$n_i(c) = (1/\pi) \cdot \text{arcctanh} \delta_i(c).$$  \hspace{1cm} (15)

where $k = 0.272 \text{ eV}$, $p = \Phi_{m} - \chi_i$; energy of surface states $\xi_i \cdot E_g$; $\xi_i = 0.3 \; (0.5; 0.7)$; barrier width $\lambda = 3\eta \; \text{Å}$, $\eta = 0.5 - 2.0$.

3. Methods and materials

The microcurrents in Si diodes and Schottky barrier diodes based on SiC and Si–Cr were measured by the method [18]. The measurement circuit is shown in Figure 2. Similar schemes are used to measure ultra-low currents.

![Figure 2. Production of single crystals, silicon carbide films, analysis of current-voltage characteristics of conventional silicon diodes and Schottky barrier diodes.](image)

4. Results

The Schottky barrier model nonlinear in the concentration of surface states is presented in [12, 19]. The approach proposed in [12] gives higher values of the Schottky barrier. At the low defect concentrations lead to better agreement with the experimental data than the classical Bardin – Schottky – Mott formula [12, 13].

It was also shown in [13, 19, 22] that “ordinary” heterojunctions based on SiC solid solutions of n-SiC/p-(SiC)1-x(AlN)x (n-p junction) type have similar characteristics and similar volt-ampere characteristics with diodes based on SiC with a Schottky barrier Me/(SiC)1-x(AlN)x (Me=Al; Ti; Cr; Ni). The calculated and experimental heights of the Schottky barriers are given in Table 1, respectively.

| Table 1. Schottky Barrier Heights for different metals |
|---------------------------------|
| Metal | Al (eV) | Ti (eV) | Cr (eV) | Ni (eV) |
| Theory | 1.74 | 1.90 | 1.78 | 2.24 |
| Experiment | 1.78 | 1.85 | 1.98 | 2.16 |
The calculated values are consistent with experimental data [12].

The value of the Schottky barrier of SiC-based diodes can also be experimentally obtained using the regimes of small signals on alternating current when removing the current volt-ampere characteristics according to a hybrid equivalent circuit [18].

A comparison of the volt-ampere characteristics of various types of diodes is shown in Figure 3. An essential difference between Schottky diodes is revealed here (Figure 3a). The diode type is 1N5822, with a current of 2A at a voltage of 0.4V and 1N5819 at a voltage of 0.6V from conventional Si–p–n junctions. For silicon diodes of type 1N5408, we have a current of 2A at a voltage of 0.85V and for 1N4004 at a voltage of 1.2V. It can be seen that Schottky diodes at the same operating currents have a lower voltage drop at the junction in the direction of direct connection, as a result of which their temperature heating, power loss, and reliability are increased.

Figure 3 (a) shows that the two upper branches belong to ordinary diodes, the two lower ones to diodes with a Schottky barrier [18]. Figure 3 (b) shows the experimental I–V characteristics of Schottky diodes with voltages up to 4V, where different charge transfer mechanisms appear (direct (a) and (b) – the theory for different ideality coefficients). The calculated straight lines in the range 01–0.5 V correspond to the direct volt-ampere characteristics of the CREE Schottky diodes of the CREE type in the range 0.5–0.9 V obtained at different temperatures (Figure 3c) [20].

![Figure 3](image-url)
5. Conclusion
Thus, the experimental data are in work, and the volt-ampere characteristics of ordinary diodes and diodes with Schottky barriers are calculated. The mechanisms of charge transfer at different ideality coefficients are revealed. The results obtained are of great practical importance in modern power, extreme micro-nano electronics.

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