Production of Single Crystals, Films and Characteristics of Schottky Diodes Based on 4H-SIC and its Solid Solutions

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***Abstract* – The article deals with the methods for producing silicon carbide (4H-SiC) mono-crystals and films using the Schottky barrier. A nonlinear model of the Schottky barrier height and a composite model for the CVC of the total emission current were developed. An induction heating method for producing SiC monocrystals at 2000-2500$0^0$C was developed. On the basis of the full-scale model of this method, a patented unit for producing perfect SiC monocrystals was designed [1]. Models of thin SiC film growth were analyzed.**

Keywords – silicon carbide monocrystals; production of thin films; Schottky barrier height; SiC-AlN-based CVC diodes; sublimation; SiC-AlN solid solutions.

I. Introduction

Growing of silicon carbide monocrystals for semiconductor production is a complicated technical task [1,2]. The main problem is the lack of a liquid phase at technically achievable pressures and high synthesis temperatures. The most common method for growing semiconductor silicon carbide single crystals is sublimation, i.e. evaporation and condensation. This method is used both for the production of abrasive material and for growing single crystals used for semiconductor electronics. The idea of the method is well known [1] and simple. It is based on the transfer of materials from a hot source (charge) to the seed with a lower temperature. Sublimation growth occurs at temperatures varying from 1,800 to 2,600 °C. The development of thin-film technologies, including those based on SiC, contributed to micro- and optoelectronics. When growing films with complex structures, it is necessary to experimentally select both the material and the structure of the substrates, as well as technological parameters of the epitaxy process.

In order to study sublimation, a full-scale model of induction heating was developed. It can be used for producing silicon carbide single crystals. The models describing thin film growth are also presented.

II. Methods and materials

1. The model of an induction heating chamber for growing perfect SIC single crystals

In [2, 10], equations for modeling the growth and distribution of temperature fields in the growth chamber were obtained. The unit with induction heating for growing silicon carbide single crystals was described (Figure 1).

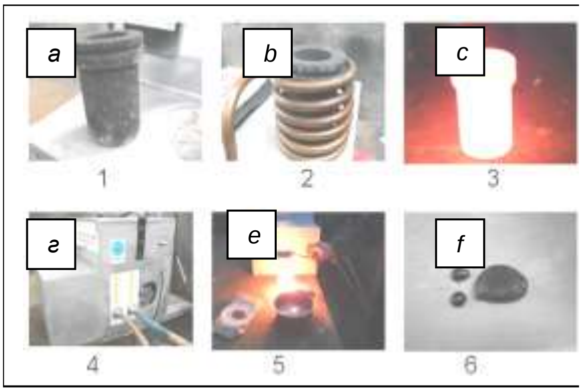

Fig. 1. Device for producing monocrystals from refractory materials: graphite pot (a), induction coil (b), melt pot (c), general view (d), melt extraction (e), melt cooling (f)

The unit [1] consists of a graphite pot, an induction coil, and a water cooling system. Refractory blanks were used to test the unit. The resulting melt in a volume of 10-20 cm^3 was poured into prepared forms at a temperature of about 2000° C. During the induction heating, ferromagnetic properties of the system changed (e.g, additional inductance). To control the heating process and maintain maximum efficiency of the system, it is necessary to change generator frequency in order to maintain the operating resonant frequency of the circuit. Modern powerful IGBT transistors were used. They are able to monitor and change the output frequency. For example, mid-frequency HDTV transistors can change the resonant frequency 20 times (up to 2000%) from 1 kHz to 20 kHz. This approach makes performance characteristics of the unit unique. The model was implemented and tested using refractory materials (Figure 1).

2. Production of SiC films and solid SiC-based solutions [3–7].

Silicon carbide films can be produced from semiconductor materials by various methods [4-6]. One of the most common methods for producing thin SiC films is chemical deposition of mixtures of silane and hydrocarbons, organosilicon compounds from the gas phase in a hydrogen stream [4, 7].

This technology is sued to produce high quality SiC epitaxial layers. However, the disadvantage of this method is high temperatures of the epitaxy process. Therefore, studies of the low-temperature synthesis of thin SiC films by vacuum laser ablation and analysis of the effect of substrate temperatures on the structure and morphology of the film surface [4] helped produce thin SiC films on a uniform silicon single crystal by laser evaporation in the vacuum for a powder target [5].

To produce solid solutions (SiC) 1-x (AlN) x, the parameters of magnetron sputtering are important. To this end, studies were carried out [6, 7] to identify dependence of the speed and sputtering coefficient on ion flux density, ion energy and cluster sizes. It was identified that calculation results correlate to experimental data.

3. The method for producing SiC-AlN and AlGaN/GaN

To produce microwave semiconductor devices based on wide-gap heterosystems, the $(SiC)_{1-x}(AlN)_x$ (SiC) systems are of interest [7]. Large band-gap widths and breakdown voltage Upr> 100V at high electron density make these hetero-systems very promising for producing high-power microwave devices. In [8, 9], manufacturing techniques for producing AlGaN / GaN using ion beam etching were described. They are used to to obtain an insulation depth of up to 100 nm. Current-voltage characteristics of the transistor structures are described. When irradiated with reactor neutrons with an energy of up to 4 MeV, drain current and output power of the transistor fall by 10%. The operating frequency gain of the current and power increases by 20-25%.

4. Models of deposition of thin SiC and AlN films and structures

At present, the issues of growth of thin films of wide-gap materials are understudied. Let us analyze two new models of thin film deposition [3,4,11].

4.1 The deposition of SiC-AlN films on the target with area S [3,4]. The surface barrier structures on the $(SiC)_{1-x}(AlN)_x$ n-type solid solution films are produced on 4H-SiC substrates by high-frequency (13.56 MHz) magnetron sputtering of composite targets. The values of sputtering coefficients are calculated by changing the weight of the target after sputtering:

$$S = \frac{26{,}6}{AI_m t} \tag{1}$$

where m is the change in target mass (mcc), I_m is the current on the target (μA), t is the sputtering time (h), A is the mass number of the target atom.

The threshold energy of separation of the atom from the surface is determined by the energy of sublimation of the substance. As a result, the sputtering rates of SiC and AlN targets are determined to produce films of a specific composition.

4.2 The quantum-static model of film formation [11,12]. In the quantum-static model of film growth on crystalline substrates, the growth rate is calculated by the integral equation for the gap (Δ) – the average condensate field:

$$\Delta = -\sum V(kk)\frac{\Delta}{\sqrt{\varepsilon^2+|\Delta|^2}}\, th\frac{\sqrt{\varepsilon^2+|\Delta|^2}}{2\Theta}\ . \tag{2}$$

V(kk) – Fourier transform of potential energy of interaction of a pair of particles, ε – renormalized system excitation energy, $\Theta = k_Б T$, k_b – Boltzmann constant.

Numerical solution of equation (2) with respect to Δ allows it to find the growth rate and other parameters of film growth.

4.3 The modified Schottky barrier model. Let us consider the Schottky barrier model with defect states localized in the contact area [19] (N_i=c·10^{13}см$^{-2}$·эВ$^{-1}$; c=0-30, where c is concentration of units 10^{13}см$^{-2}$·eB^{-1}). Along with the concentration of defects N_i, occupation numbers $n_x(c)$ are introduced. They are determined by the type of Hamiltonian system (the Andersen Hamiltonian). This approach produces higher values of the Schottky barrier even for small N_i (N_i<10^{13}см$^{-2}$·эВ$^{-1}$ [7,17]) and contributes to better correlation to the experimental data. In this model, the barrier height Φ_B^x is determined by formula [15, 17]:

$$\Phi_B^x(c) = \Phi_m - \chi + \Delta\Phi_x(c)\,,$$

$$\Delta\Phi_x(c) = 4\pi\left(e^2/4\pi\varepsilon_0\varepsilon\right)\lambda N_i n_x(c)\,. \qquad (3)$$

Φ_m – metal work, χ – electronic affinity, $\Delta\Phi_x(c)$ – potential barrier due to electron tunneling between the metal and localized quasi-levels (states E_i), λ –thickness of the double layer with dielectric constant $\varepsilon_0\varepsilon$, N_i – density of isolated states of the defect, $n_x(c)$ – fnumber of occupation of the localized quasi-level E_i with half width $\Gamma=\pi\rho U^2$ (U – energy of hybridization of metallic and localized states), ρ – constant density of states of the metal, E_F – fermi energy. Then the semiconductor which is in contact with the metal is characterized by surface defect states |*d*>, whose energy E_i is localized in the forbidden zone. Interaction of the level |*d*> and the metal can be described by Andersen Hamiltonian [18].

For the potential Schottky barrier height Φ_B^x and occupation numbers $n_x(c)$ by (3) and (5), we have [10,13]:

$$\Phi_B^x(c) = p + k\eta c 2 n_x(c)\,,$$

$$\Gamma\delta_x(c) = p - (1-\xi_i)\mathrm{E}_g^x + k\eta c(1-c\nu)\,, \qquad (4)$$

$$n_x(c)=(1/\pi)\cdot arccot\delta_x(c). \qquad (5)$$

k=0,272 eV, $p=\Phi_m-\chi$; surface state energy is $E_i=E_g\xi_i$, ξ_i = 0.3 (0.5; 0.7); barrier width is λ=3ηÅ, η=0.5–2.0; in approximation c^2 at $2n_{x0}\approx 1-c\nu$, we have (5), where ν is the decomposition coefficient taking values from 0 to 1/30.

The results of calculation of the Schottky barrier height as a function of the parameters of the nonlinear model ξ_i, x and c [17] by (4), (5) are presented in Figures 2 and 3.

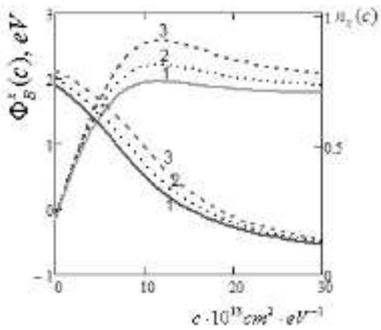

Fig. 2. Shottky barrier and occupation numbers as functions of defects concentration for the n-al / p (sic) 1-x (aln) x system and for the value of energy of defects ei≈0.5egx, at x = 0.2; 0.5; 0.7 for curves 1, 2 and 3, respectively

At ν = 0, formulas (4) - (5) produce values that are close to linear ones with respect to the model *c* (BSN) [15]; at $c(1-c\nu)=0$ in (5), the model BSN coincides with the model BS.

Figure 2 presents the analysis results for the dependence of the values of the Schottky barrier Φ_B^x and n_x on the concentration of defects *c* (BSN), for values $E_i\approx 0.5E_g^x$ [15], at x= 0.2; 0.5; 0.7. Figure 3 shows the dependences of the Schottky barrier height as a function of composition x.

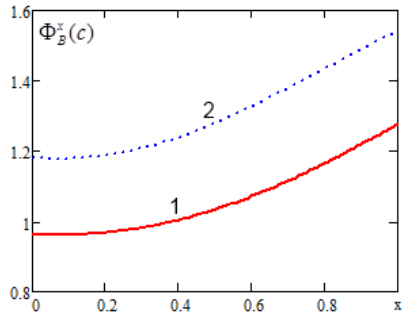

Fig. 3. Schottky barrier height as a function of composition x for n-al/p-(sic)1-x(aln)x at c=4; e1=0.3eg (curve 1) and e2=0.5eg (curve 2)

4.4 Data on the values of the Schottky barriers in SiC film-based diodes. In [4], using the values of photocurrent of the produced structures Me/$(SiC)_{0.4}(AlN)_{0.6,}$ the height of the Schottky barriers for metals (Me) Al, Ti, Cr, Ni: 1,78; 1,85; 1,98; 2,16 eV was determined. These values are consistent with the calculations for the modified Schottky barrier model. Φ^X_B(C): 1,74; 1,90; 1,78; 2,24 eV [10,13] at Ni= 6·10^{13}cm^{-2}·eV^{-1} (c=6). The values for Cr fall out of the total number due to the initial value for its work function. The values are in good agreement with the results of the experiments.

5. The CVC of SiC-based diodes

In heterojunctions n-SiC/p-$(SiC)_{1-x}(AlN)_x$ at the boundary of the transition into a region with a high density of charge carrier states, a resonant quasi-level $E_F$occurs. The current carriers penetrate through the barrier. The current passage through Φ_g^x will be thermionic (te), field (p) or thermofield (*tp)* emission depending on voltage *U*. This explains qualitative similarity of the CVC of diodes with the Schottky barrier and usual *p-n* junctions [16]. In these cases, to describe the current-voltage characteristics of SiC-based diodes in a wide voltage range ($0 < U < 5 \div 15$B), we developed a composite current-additive model. In this model, in the region of low voltages ($0 < U < 0.5$B), current is determined by thermionic emission. Field emission manifests itself in the field of stresses $0.5 < U < 2.5B$. Thermal field emission is observed in the stress region $2.5 < U < 5B$ [7,16].

In the field of low stresses ($0 < U < 0.5B$), the current of thermionic emission will be [16]

$$I_{te}(U,x) = I_{ss}^x\left[exp\left(\frac{qU}{nkT}\right) - 1\right],$$

$$I_{ss}^x = sA^*T_i^2\, exp\left(-\frac{\Phi_B^x(c)}{mkT}\right), \qquad (6)$$

where I_{ss}^x – saturation current, s – contact area (2÷5 mm^2), x – composition, A^* – Richardson constant equal to $120(m_e^*/m_e)\ A/cm^2\cdot K^2$; q – electronic charge, n and m – ideality factors.

Taking into account the experimental data [7], field emission which manifests itself in the field of stresses $0.5 < U < 2.5B$, can be presented as

$$I_p(U,x) = I_p^x \, exp\left(\frac{qU}{n_1 E_{00}^x}\right),$$

$$I_p^x = sA_i^{**} T_i^2 \, exp\left(-\frac{\Phi_B^x(c)}{E_{00}^*}\right). \quad (7)$$

n_1 - ideality factor for $I_p(U,x)$; A_i^{**} – coefficient associated with Richardson constant A^*, dependent on the initial material [16]; $E_{00}^* = m_1^i E_{00}$ ($E_{00} \approx 20$мэВ) – factor m_1^i and characteristic energy of the material which can be determined from experimental data.

For thermal field emission in the region of voltages $2.5 < U < 5B$ according to [16] we have:

$$I_{tp}(U,x) = I_{tp}^x \, exp\left(\frac{qU}{n_2 E_0^x}\right),$$

$$I_{tp}^x = sB_i T_i^2 \, exp\left(-\frac{\Phi_B^x(c)}{E_0^*}\right), \quad (8)$$

where n_2 and m_2^i – ideality factor for $I_{tp}(U,x)$; $E_0^* = m_2^i E_0$, $E_0 = E_{00} ct\square(E_{00}/kT)$; c – concentration of surface defects; $i = 1,2,3,4$ and E_0 – characteristics energy of the material. Dependence $T_i{}^2$ in (16) was calculated from the experimental data [7].

III. Results

1. A unit for producing single crystals from refractory materials has been designed and tested. The unit with a controllable induction heating system for growing perfect crystals helps produce the following types of samples and the simplest products (Figure 4).

a) b) c)

Fig. 4. Samples: ceramics(a), silicon carbide (b) sic -diodes-based products (c)

2. Data on the methods for producing SiC film and solid solutions were presented.

TABLE I. COMPARISON OFEXPERIMENTAL DATA AND CALCULATION VALUES OF THE SCHOTTKY BARRIERS

Metal	*Al*	*Ti*	*Cr*	*Ni*
Experimental data, eV	1,78	1,85	1,98	2,16
Calculation results, eV	1,74	1,90	1,78	2,24

3. The values of the Schottky barriers in SiC film-based diodes were calculated. They are in agreement with the experimental data. The calculated values of the Schottky barriers presented in Table 1 are in agreement with the experimental data.

4. Models of thin SiC film formation were suggested.

IV. Conclusion

The paper presents the method of induction heating to produce single SiC crystals at temperatures varying from 2000 to 25000 ^{0}C. On the basis of the full-scale model of this method, a patented unit was designed for producing perfect single SiC crystals.

Two models for producing SiC films and heterostructures were analyzed. The parameters of the film deposition process were estimated: composition, film growth rate, and Schottky barrier values in metal-semiconductor structures.

The modified Schottky barrier model based on 4H-SiC and its solid solutions was developed.

The theory of IUC diodes based on silicon carbide for composite (additive) emission current through the Schottky barrier was developed.

The development and production of diodes, LEDs, transistors, microcircuits and special devices based on silicon carbide structures and films are an elemental base of power extreme microelectronics of a new generation.

Currently, devices based on 4H-SiC with a very high level of output power [14] are being developed. Studies of IUC degradation at high current densities are being conducted (see, for example, [15]).

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