

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 December 2000 (28.12.2000)

PCT

(10) International Publication Number
WO 00/79570 A2

(51) International Patent Classification⁷:

H01L

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(21) International Application Number:

PCT/US00/15155

(22) International Filing Date:

1 June 2000 (01.06.2000)

(81) Designated States (national): AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW.

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09/339,510

24 June 1999 (24.06.1999) US

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

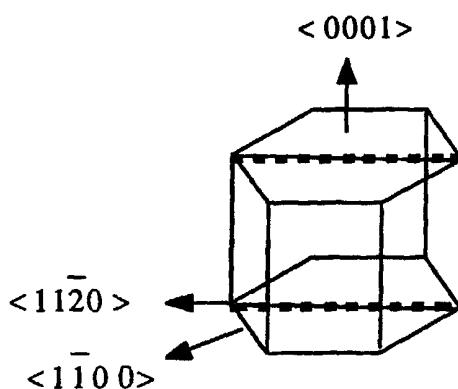
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Published:

— Without international search report and to be republished upon receipt of that report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SILICON CARBIDE EPITAXIAL LAYERS GROWN ON SUBSTRATES OFFCUT TOWARDS <1100>



WO 00/79570 A2

(57) Abstract: A silicon carbide epitaxial film, grown on an offcut surface of a SiC crystalline substrate of hexagonal crystal form, having an offcut angle of from about 6 to about 10 degrees, toward the <1100> crystalline direction of the substrate. The resultant silicon carbide epitaxial film has superior morphological and material properties.

SILICON CARBIDE EPITAXIAL LAYERS GROWN ON SUBSTRATES**OFFCUT TOWARDS $<1\bar{1}00>$**

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BACKGROUND OF THE INVENTION

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Field of the Invention

This invention relates to silicon carbide (SiC) epitaxial layers grown on substrates offcut towards $<1\bar{1}00>$, to devices comprising such SiC epitaxial layers, and to a method of
15 making such SiC epitaxial layers.

Description of the Related Art

High doping concentrations are required to form low specific contact resistances in SiC ohmic
20 contacts. Low ohmic contact resistances improve the performance of SiC devices. Conventional SiC homoepitaxy is performed on SiC substrates offcut towards the $<11\bar{2}0>$ crystalline direction. N-type doping concentrations are typically in the range of 10^{18} atoms $\cdot \text{cm}^{-3}$, with some reports describing doping levels $>10^{19}$ atoms $\cdot \text{cm}^{-3}$, but higher doping
25 concentrations and more efficient dopant incorporation (of both n-type and p-type dopants) are desired. Epilayers may offer lower defect densities and more controlled doping compared to substrate doping or dopant implantation into the substrate.

It is also desirable to provide a more uniform surface structure on the epitaxial layer surface. A uniform surface should facilitate the desired removal of material during device fabrication. A

uniform epitaxial structure increases the ability to accurately predict how much material is removed during etching, and both the inter-wafer and the run-to-run etching variations are reduced. Smooth and uniform surfaces, especially in cases such as evaporated Schottky contact metals, will lead to improved device performance.

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It is also desirable to have a more uniform surface to facilitate oxide formation and to reduce the density of interface trap states. Further, a more uniform epitaxial surface may reduce surface disparities that can lead to undesirable electric field emitter sites and ultimately premature oxide breakdown. Improved oxide properties will lead to improved device and

10 passivation performance.

In SiC MOSFETs, the epitaxial layer comprising the channel can be polished to remove the steps on the surface that alter channel mobility (see S. Scharnholz, E. Stein von Kamienski, A. Golz, C. Leonhard, and H. Kurz, Material Science Forum, **264-268**, 1001 (1998)). The polish

15 will be more uniform with a more uniform step structure, and MOS performance will improve.

The zig-zagged step structure found on SiC offcut towards the $<11\bar{2}0>$ is also likely to have a higher density of bonding disparities including dangling bonds that may cause high interface trap densities. Additionally, the large surface area exposed to ambient on the zig-zagged $<11\bar{2}0>$ - offcut epitaxial surface may make this surface more reactive and prone to

20 undesirable impurity incorporation.

It therefore is an object of the invention to provide an SiC material that minimizes or overcomes the problems of conventional SiC discussed hereinabove.

25 It is another object of the invention to provide a method of making SiC material of such improved character.

Other objects and advantages of the invention will be more fully apparent from the ensuing disclosure and appended claims.

SUMMARY OF THE INVENTION

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The present invention in one aspect relates to an epitaxial SiC film, grown on an offcut surface of a SiC substrate having a hexagonal crystal structure, with the offcut surface having an offcut angle of from about 6 to about 10 degrees, and the crystallographic direction of the offcut surface being towards one of the six equivalent $<1\bar{1}00>$ directions of the substrate \pm 7.5 degrees.

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The invention in another aspect relates to a silicon carbide article, comprising:

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a SiC substrate of hexagonal crystal form, with an offcut surface having an offcut angle of from about 6 to about 10 degrees, and the crystallographic direction of the offcut surface being towards one of the six equivalent $<1\bar{1}00>$ directions of the substrate \pm 7.5 degrees; and

20

an epitaxial SiC film, grown on the offcut surface.

The present invention relates in yet another aspect to silicon carbide epitaxial material, grown on a (0001) 4H-SiC crystalline substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate.

25

The invention relates in another aspect to a 4H-SiC epilayer film grown on a (0001) 4H-SiC substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate, wherein the epilayer film has a LEED $(0\bar{1})$ beam intensity profile substantially as shown in Figure 2, discussed more fully hereinafter.

A further aspect of the invention relates to a 4H-SiC epilayer film grown on a (0001) 4H-SiC substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate, wherein the epilayer film has an average root mean square roughness not exceeding about 2.0 nanometers,
5 and preferably less than 1 nanometer.

Another aspect of the invention relates to a silicon carbide article comprising a 4H-SiC epitaxial material on a (0001) 4H-SiC single crystal substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate.

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A still further aspect of the invention relates to a silicon carbide article comprising a 4H-SiC epilayer film grown on a (0001) 4H-SiC substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate, and having a LEED $(0\bar{1})$ beam intensity profile substantially as shown in Figure 2 hereof.

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In a still further aspect, the invention relates to a silicon carbide article comprising a 4H-SiC epilayer film grown on a (0001) 4H-SiC substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate, and having an average root mean square roughness not exceeding about 2.0 nanometers, and preferably less than 1 nanometer.

20

As used herein, the term "silicon carbide article" includes a silicon carbide epitaxial film on a silicon carbide base material. The silicon carbide base material may constitute a substrate body (e.g., wafer) formed of silicon carbide, or the silicon carbide base material may comprise an intermediate layer on which the silicon carbide epitaxial film is formed, for example as part of a
25 multilayer microelectronic device (e.g., circuit) structure or as a part of some other structural body or form including the silicon carbide epitaxial film on the silicon carbide base material.

Concerning such device applications, the SiC films of the present invention may be employed for a wide variety of microelectronic devices or device precursor structures, including, without limitation, Schottky and p-n diode rectifiers, SiC photo-diodes and SiC light emitting diodes, switching devices, including field effect transistors (e.g., JFET, MOSFET and MESFET devices), monolithic integrated SiC operational amplifier chips, digital logic gates, latches, flip-flops, binary counters, half adder circuits, non-volatile random access memory (NVRAM) arrays and other SiC digital integrated circuits.

10 A broad method aspect of the invention relates to a method of forming a silicon carbide epitaxial film, comprising depositing such film on a silicon carbide crystalline substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate.

15 In another method aspect, the invention relates to a method of forming a silicon carbide epitaxial film, comprising depositing such film on a (0001) 4H-SiC crystalline substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate.

20 A further method aspect of the invention relates to a method of forming a silicon carbide epitaxial film, comprising growing such film on a (0001) 4H-SiC crystalline substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate, wherein the growing step comprises:

introducing a carrier gas, a vaporized silicon-containing material and a vaporized carbon-containing material into a growth chamber; and

25 maintaining the carrier gas, silicon-containing material and carbon-containing material flows and temperature condition for a time sufficient to grow a film of desired thickness.

The silicon-containing material and the carbon-containing material in the above method may comprise a single source material in which the source reagent contains silicon and carbon, in a single compound, adduct or coordination complex.

5 Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

10 Figure 1 is a schematic representation of a hexagonal SiC crystal structure showing the respective directions of such crystal structure.

Figure 2 shows a LEED (01̄) beam intensity profile produced by directing an incident 80eV beam onto the center (squares) or 1 mm from the edge (triangles) of an 11 μm thick epilayer 15 grown on 4H-SiC (0001) offcut $8^\circ \rightarrow <1\bar{1}00>$, with the inset in Figure 2 showing a typical 1×1 LEED pattern at $E_i = 80$ eV.

Figure 3 shows the AFM scan for an epilayer grown on 4H-SiC (0001) offcut $8^\circ \rightarrow <11\bar{2}0>$.
20 Figure 4 shows an AFM scan for an epilayer grown on 4H-SiC (0001) offcut $8^\circ \rightarrow <1\bar{1}00>$.

Figure 5 shows variation of donor concentration measured by CV analysis via variation of C/Si (constant partial pressure N_2 , triangles) and variation of partial pressure N_2 (constant C/Si, squares) for films grown on 4H-SiC (0001) offcut $8^\circ \rightarrow <1\bar{1}00>$.

25 Figure 6 shows variation of Al concentration (SIMS analysis) via variation of TEA flow for films grown on 4H-SiC (0001) offcut $8^\circ \rightarrow <1\bar{1}00>$.

Figure 7 shows a SIMS nitrogen profile of a 15.5 μm thick epilayer grown on 4H-SiC (0001) offcut $8^\circ \rightarrow <1\bar{1}00>$.

Figure 8 shows the bonding configuration of the $<1\bar{1}00>$ surface of a (0001) 4H-SiC material.

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**DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED
EMBODIMENTS THEREOF**

10 While the ensuing description of the invention is directed primarily to silicon carbide epitaxial films formed on 4H-SiC substrate materials, it will be appreciated that the utility of the invention is not thus limited, and that the invention broadly contemplates the formation of epitaxial silicon carbide on other types of silicon carbide substrates, such as exist in a great variety of hexagonal (H), rhombohedral (R) and cubic (C) crystal forms, among the more than 15 200 polytypes of silicon carbide. Illustrative polytypes include 4H-SiC, 6H-SiC, 15R-SiC and 3C-SiC. 4H-SiC and 6H-SiC are presently preferred, with 4H-SiC being most preferred.

In this respect, it is to be noted that the offcut epitaxial SiC growth surface is described herein for various hexagonal crystallographic forms of SiC, in corresponding hexagonal directional 20 notation. For other crystalline forms of SiC, e.g., rhombohedral, cubic, etc., suitable offcut surfaces may be analogously described with respect to their planes, angles and directions, in equivalent crystallographic directional notations that are specific to such other crystalline forms.

25 The present invention contemplates the formation of device quality SiC films on corresponding substrates. In the case of 4H-SiC, the substrate has a planar growth surface (interface) that is offcut, i.e., inclined with respect to the axis of a basal plane thereof, with (I) an angle of inclination between the planar growth surface and the axis of the basal plane (offcut angle) from about 6 to about 10 degrees, more preferably from about 7 to about 9 degrees and most 30 preferably about 8 degrees, and (II) the crystallographic direction of the inclined planar growth

surface being towards one of the six equivalent $<1\bar{1}00>$ directions of the substrate \pm 7.5 degrees (i.e., such direction being within an arc range of 15 degrees that is centered on the $<1\bar{1}00>$ direction as the midpoint of such range).

5 The epitaxial SiC film formed on the substrate preferably is an SiC film of the same polytype as the substrate, and the epitaxial film is suitably homoepitaxially deposited on the substrate interface surface.

The silicon carbide films of the present invention possess a smooth surface morphology, within 10 an edge exclusion area (the edge exclusion area generally having an edge thickness dimension on the order of about 3 millimeters). Such smooth surface is characterized by a root mean square roughness not exceeding about 2 nanometers (20 Angstroms) in magnitude, and more preferably such smooth surface has a root mean square roughness of less than about 1 nanometer (10 Angstroms) in magnitude. All root mean square values of surface roughness 15 herein refer to root mean square roughness values as measured on a $20 \mu\text{m} \times 20 \mu\text{m}$ area using a Digital Instruments Dimension 3000 atomic force microscope with a probe tip radius of 5 nanometers (nm).

Such silicon carbide epitaxial films also have a substantially uniform thickness and a low defect 20 density (it being recognized that different polytypes have differing varieties of and susceptibility to defects; e.g., triangle defects are specific to 4H-SiC) that is compatible with microelectronic device applications. The silicon carbide film is amenable to doping with p-type dopants and/or n-type dopants, which may selectively be incorporated in the film, or selected region(s) thereof, at any suitable dopant concentration, e.g., a concentration of from 25 about 1×10^{13} to about 1×10^{21} atoms $\cdot \text{cm}^{-3}$. For example, n-type doping can be carried out using nitrogen as the dopant species and gaseous nitrogen as the dopant source gas. Techniques such as site competition epitaxy can be used to enhance the incorporation of nitrogen so that heavily-doped epitaxial layers can be fabricated, e.g., for ohmic contacts. P-

type doping can be carried out using aluminum as the dopant species and trimethylaluminum or triethylaluminum as the dopant source reagent, or alternatively using boron as the dopant species and diborane or other boron-containing precursor as the dopant source reagent. N-type and p-type doping may be selectively used to form corresponding p-n junctions in the film material.

5 The present invention overcomes the problems of prior art SiC materials discussed in the Background of the Invention section hereof, by the provision of SiC epitaxial growth on SiC substrates, as more fully shown hereinafter with reference to (0001) 4H-SiC substrates, that are
10 offcut towards the $<1\bar{1}00>$ direction instead of the commonly used offcut direction of $<11\bar{2}0>$. Growth on substrates offcut towards the $<1\bar{1}00>$ direction of the SiC crystal permits substantially improved morphological and material properties to be achieved in relation to other growth orientations. Such improved properties include a higher level of dopant incorporation, and the formation of a significantly more uniform surface structure facilitating
15 etching, polishing and oxide formation.

By way of further background toward understanding the substantial advance in the art achieved by the present invention, substrate crystalline orientation is a key factor in determining the quality of SiC epitaxial layers formed by chemical vapor phase epitaxy. Early investigation of
20 SiC growth determined that growth on 6H-SiC (0001) substrates yielded 3C-SiC layers riddled with double positioning boundaries (DPB) unless very high growth temperatures (>1500 °C) were used (see V. J. Jennings, A. Sommer, and H. C. Chang, J. Electrochem. Soc. 113, 728 (1966); and S. Nishino, H. Matsunami, and T. Tanaka, J. Crystal Growth 45, 144 (1978)). Subsequent work showed that very high quality homoepitaxial 6H-SiC films could be produced
25 using growth temperatures as low as 1200°C if the substrate was offcut several degrees from the (0001) plane (see N. Kuroda, K. Shibahara, W.S. Woo, S. Nishino, and H. Matsunami, Ext. Abstr. The 19th Conf. On Solid State Devices and Materials (Tokyo, 1987) p. 227; and H. S. Tong, J. T. Glass, and R. F. Davis, J. Appl. Phys. 64, 2673 (1988)). The offcut produces a

series of steps and terraces on the SiC surface that promotes lateral growth (step flow growth).

In this manner, the epilayer replicates the stacking order of the substrate, and high quality homoepitaxial growth ensues.

5 While most of the work in SiC epitaxy has focused on substrates offcut 4-8° towards one of the six equivalent $\langle 11\bar{2}0 \rangle$ crystalline directions, the effect of alternative substrate offcut directions has remained a critical, but less studied, aspect of SiC epitaxy. Studies of SiC epitaxial growth on alternative substrate orientations have focused on growth on $\{11\bar{2}0\}$, $\{1\bar{1}00\}$, or $\{01\bar{1}4\}$ surfaces (see A. A. Burk, D. L. Barret, H. M. Hobgood, R. R. Siergiej, T. T. Braggins, R. C. 10 Clarke, W. G. Eldridge, C. D. Brandt, D. J. Larkin, J. A. Powell, and W. J. Choyke, *Inst. Phys., Conf. Ser.* **137**, 29 (1993); A. Yamashita, W. S. Woo, T. Kimoto, and H. Matsunami, *Jpn. J. Appl. Phys.* **31**, 3655 (1992); and W. Si, M. Dudley, H.-S. Kong, J. Sumakeris, and C. Carter, *J. Electronic Matl.* **26**, 151 (1997)). Epitaxial growth on 6H-SiC (0001) substrates offcut $\leq 4^\circ$ towards the $\langle 1\bar{1}00 \rangle$ direction (denoted 6H-SiC (0001) offcut $X^\circ \rightarrow \langle 1\bar{1}00 \rangle$) was 15 previously studied, but the surface possessed large-scale step bunching which appeared as striations when viewed using optical microscopy (see S. Karmann, W. Sutrop, A. Schoner, M. Schadt, C. Haberstroh, F. Englebrecht, R. A. Stein, and S. Leibenzeder, *J. Appl. Phys.* **72**, 5437 (1992)) and exhibited degraded morphology compared to material offcut towards $\langle 11\bar{2}0 \rangle$ (N. Kuroda, et al., *ibid.*). The striations degraded into rough 3D growth as thicker 10 μm layers 20 were grown in a similar study (see T. Ueda, H. Nishino, and H. Matsunami, *J. Crystal Growth* **104**, 695 (1990)). The magnitude of the offcut angle also plays a key role in 4H-SiC epilayer growth. Reduction of 3C-SiC triangular inclusions was obtained on substrates offcut 8° from the (0001) plane towards $\langle 11\bar{2}0 \rangle$ for 4H-SiC homoepitaxy, compared to substrates offcut by 25 4° (see A. Yamashita, et al., *ibid*; J. A. Powell and D. J. Larkin, *Phys. Stat. Solidi B* **202**, 529 (1997) and references therein; and T. Kimoto, A. Itoh, and H. Matsunami, *Appl. Phys. Lett.* **66**, 3645 (1995)).

The present invention embodies the use of silicon carbide substrates, e.g., (0001) SiC substrates, offcut towards the $<1\bar{1}00>$ crystalline direction for SiC epitaxial growth. In contrast to the literature in the art to date and the teachings in U.S. Patent No. 4,912,064 that describe the $<11\bar{2}0>$ as the optimal offcut direction for SiC epitaxial growth, we have found

5 that surfaces offcut towards the $<1\bar{1}00>$ direction are superior to surfaces offcut towards the $<11\bar{2}0>$ direction. More specifically, we have found that device quality SiC films can be readily produced on 4H-SiC substrates characterized by an offcut angle of from about 6 to about 10 degrees, more preferably from about 7 to about 9 degrees, and most preferably about 8 degrees, with the direction of the offcut surface being towards one of the six equivalent 10 $<1\bar{1}00>$ directions \pm 7.5 degrees (preferably \pm 5 degrees, more preferably \pm 2.5 degrees, and most preferably \pm 1.5 degrees).

By way of specific example, high quality 4H-SiC epilayers can be grown on (0001) 4H-SiC substrates offcut $8^\circ \rightarrow <1\bar{1}00>$.

15

The invention permits unexpectedly higher doping levels to be achieved on the $<1\bar{1}00>$ offcut epilayers compared to the $<11\bar{2}0>$ offcut epilayers for identical doping deposition conditions. Furthermore, a substantially more uniform surface structure is produced, providing correspondingly improved etching, polishing and oxide formation.

20

The crystal directions of hexagonal SiC are illustratively shown in Fig. 1 with respect to the $<0001>$ (c-axis) direction. The invention will now be described with reference to the formation of a 4H-SiC epitaxial layer on an offcut (0001) 4H-SiC substrate, in accordance with a preferred embodiment of the invention.

25

The 4H-SiC epitaxial material of the invention may be formed as a layer on the offcut (0001) 4H-SiC substrate by a growth process in which silicon- and carbon-containing precursor vapor,

e.g., deriving from a mixture of silane gas and methane gas, or other silicon and carbon source reagents, optionally and preferably in a carrier gas such as hydrogen, are introduced to the growth chamber containing the offcut (0001) 4H-SiC substrate under appropriate growth conditions, e.g., of flow rates and concentration of the silicon source and carbon source reagents, elevated temperature, and appropriate pressure ranging from atmospheric to subatmospheric pressure (preferably subatmospheric pressure), to produce an epitaxial growth on the offcut growth surface of the substrate.

5 The epitaxial 4H-SiC material formed on the substrate may be grown to any suitable thickness, e.g., from about 0.002 to 400 micrometers, as may be necessary or desirable in a given application of the method and resultant film material. The film material may be grown to appropriate thickness and utilized on the substrate, or it may be separated from the substrate, e.g., by internal pressure fracturing techniques, etch removal of the substrate, or other suitable procedure, to provide a thin film body of the 4H-SiC material, as a free-standing (self-supporting) entity.

10 The 4H-SiC epitaxial material of the invention may be doped during its growth by in-situ doping techniques using appropriate n-type and/or p-type dopant species, as appropriate to the desired end use of the epilayer material. Alternatively, the epilayer material may be doped 15 subsequent to its formation, by ion implantation, diffusion or other suitable techniques.

20 The 4H-SiC epitaxial material of the invention is of superior device quality, and may be used for the fabrication of microelectronic device structures thereon and/or therein, e.g., MOSFETs, other semiconductor device structures, diodes, capacitors, memory cell architectures, etc.

25

A wide variety of SiC film formation processes may be employed in the broad practice of the invention to form the epitaxial SiC layer on the substrate, including bulk growth techniques, the modified Lely process, epitaxial growth techniques, molecular beam epitaxy, and chemical

vapor deposition. The silicon and carbon source reagents may be of any suitable type, e.g., silane as a silicon source reagent, and a hydrocarbon gas such as methane, propane, etc., as the carbon source reagent. It is also possible to utilize a single source reagent, containing both carbon and silicon atoms, as the source material for the silicon carbide film.

5

Relative to generalized processing techniques and background relating to silicon carbide film and device formation, the disclosures of U.S. Patent 4,912,064 issued March 27, 1990 in the names of H. Kong et al. for "Homoepitaxial growth of alpha-SiC thin films and semiconductor devices fabricated thereon," and U.S. Patent 5,661,074 issued August 26, 1997 in the names of

10 Michael A. Tishchler, et al. for "High brightness electroluminescent device emitting in the green to ultraviolet spectrum and method of making the same" are incorporated herein by reference in their entireties.

In one illustrative embodiment of the invention, 4H-SiC epitaxial films were grown on single

15 crystal 4H-SiC wafers oriented $8 \pm 1^\circ$ from (0001) towards either the $<1\bar{1}00>$ or $<11\bar{2}0>$. The films were grown in a horizontal quartz water-cooled reaction chamber, although other reactor configurations are possible. The 4H-SiC films were grown at 100 Torr using dilute SiH₄ and CH₄ with a H₂ carrier gas. As mentioned, other Si- and C-containing precursors can be used to produce the SiC films.

20

Growth temperatures were typically in the range of 1450 – 1550°C, and were obtained by placing the wafer on a graphite-based susceptor and heating using RF induction. Many growth system designs are possible, and can be constructed by those skilled in the art of epitaxial growth. Intentional doping was accomplished using N₂ gas to provide the n-type dopant (N) and triethylaluminum (TEA) to provide the p-type dopant (Al). Other dopant precursors, including, without limitation, PH₃, B₂H₆, TMA, and various vanadium-containing precursors can also be used.

The specific growth parameters chosen for this illustrative embodiment of the invention were those identified as optimal for growth on 4H-SiC (0001) offcut $8^\circ \rightarrow <11\bar{2}0>$; no effort was made to optimize the growth parameters for epitaxial growth on 4H-SiC (0001) offcut $8^\circ \rightarrow <1\bar{1}00>$. Suitable process conditions of temperature, pressure, and gas flows can be selected and optimized by those skilled in the art, for the desired epitaxial growth operation.

The results of the above-described growth of SiC included smooth surface morphologies for the 4H-SiC epilayers grown on both substrate orientations. No large-scale step bunching or rough 3D growth was observed, even for epilayers as thick as 15 μm .

10

Triangular 3C inclusions, commonly observed in 4H-SiC growth on substrates oriented towards $<11\bar{2}0>$, were observed on epilayers grown on 4H-SiC substrates for both offcut directions. The triangular defect densities were similar on samples with comparable epilayer thicknesses, and were located mainly at the wafer periphery for both offcut directions. The overall triangle defect density was higher on 4° offcut wafers compared to 8° offcut wafers, regardless of offcut direction.

LEED spot intensity and spot profiles were used to examine the near-surface region of 4H-SiC epitaxial films grown on substrates oriented towards $<1\bar{1}00>$, following the procedure of M. 20 Henzler, Appl. Surf. Sci. **11/12**, 450 (1962). Bright, sharp diffraction patterns, indicative of high crystalline quality, are observed; the inset in Figure 2 shows a typical 1x1 LEED pattern at an incident electron energy of 80 eV. A position-dependent study of the $(0\bar{1})$ beam spot profiles revealed superior crystalline quality across the wafer, degrading only within the 3mm wafer edge region where the triangular defect density increased.

25

The LEED $(0\bar{1})$ beam intensity profile of Figure 2 was produced by directing the incident 80eV beam onto the center (squares) or 1 mm from the edge (triangles) of an 11 μm thick epilayer

grown on 4H-SiC (0001) offcut $8^\circ \rightarrow <1\bar{1}00>$. The inset in Figure 2 shows a typical 1×1 LEED pattern at $E_i = 80$ eV.

Atomic force microscopy (AFM) analysis revealed that 4H-SiC epitaxial films grown on substrates offcut towards either $<11\bar{2}0>$ or $<1\bar{1}00>$ were very smooth, exhibiting an average RMS roughness that was always less than 0.8nm (400 μm^2 scan area). Over 20 $<1\bar{1}00>$ - oriented epilayers were studied using AFM; a data analysis is set out hereinafter for a typical subset of these growths. The RMS roughness for epilayers grown during the same growth run on both offcut directions were similar for comparable film thickness and scan size, increasing only slightly with increasing epilayer thickness.

The variation in the RMS roughness measured across the wafer was smaller for epilayers grown on substrates offcut towards $<1\bar{1}00>$. Films grown on substrates oriented towards $<1\bar{1}00>$ possessed a regular, parallel and distinct step structure whereas films grown on substrates oriented towards $<11\bar{2}0>$ exhibited a more irregular step structure. The direction of the steps on both offcut orientations was parallel to the offcut direction, consistent with step flow growth.

After taking into account the 5nm probe tip radius, an analysis of the step heights (both offcut directions) revealed that the most common step height was 0.5nm, equal to two Si-C bilayers or half the 4H unit cell height. Steps of 4 Si-C bilayers were also observed, but with less frequency than observed on epilayers grown on 4H-SiC (0001) offcut $3.5^\circ \rightarrow <11\bar{2}0>$ (epilayers grown on 4H-SiC (0001) offcut $3.5^\circ \rightarrow <11\bar{2}0>$ are described in T. Kimoto, A. Itoh, and H. Matsunami, Appl. Phys. Lett. **66**, 3645 (1995)). No evidence of larger scale step bunching could be seen when the AFM scan areas were increased.

Table I shows the average RMS and doping concentration (CV) for different thickness intentionally n-type 4H-SiC epilayers grown using identical conditions on substrates offcut 8° toward $<1\bar{1}00>$ or $<11\bar{2}0>$. The RMS average and standard deviations, shown in parentheses, were calculated from three random measurements on the wafer. Where no deviation value is presented, the RMS value is from a single point measurement near the center of the wafer. Epilayers of the same thickness were grown during the same growth run.

Table I

	3 μ m		5 μ m		15 μ m	
	$<1\bar{1}00>$	$<11\bar{2}0>$	$<1\bar{1}00>$	$<11\bar{2}0>$	$<1\bar{1}00>$	$<11\bar{2}0>$
RMS (nm) $0.5 \times 0.5 \mu\text{m}^2$	0.12	0.16	0.14 (0.02)	0.13 (0.02)	0.20 (0.01)	0.14 (0.01)
RMS (nm) $20 \times 20 \mu\text{m}^2$	0.23	0.55	0.37 (0.02)	0.27 (0.06)	0.77 (0.12)	0.68 (0.21)
$N_d (10^{16} \text{ cm}^{-3})$	5	4	6	5	9	6

10

AFM scans are shown in Figure 3 and Figure 4 for $500 \times 500 \text{ nm}^2$ areas of 15.5 μm thick 4H-SiC epilayers grown during the same growth run. Height scale on both profiles is 2 nm/division. Figure 3 shows the AFM scan for an epilayer grown on 4H-SiC (0001) offcut 8° towards $<11\bar{2}0>$, while Figure 4 shows an AFM scan for an epilayer grown on 4H-SiC (0001) offcut 8° towards $<11\bar{2}0>$.

15

In addition to good film quality, it was found that the n-type dopant incorporation was higher for films grown on substrates offcut towards the $<1\bar{1}00>$ compared to films grown on wafers offcut towards $<11\bar{2}0>$ for identical growth conditions. Table I also shows the donor concentrations (N_d) for films grown on both orientations. SIMS analysis of these samples agreed well with the CV results, indicating comparable activations for the two orientations.

Additional experiments also confirmed the trend of high doping levels on substrates offcut towards $<1\bar{1}00>$.

It is important to note that while the overall doping level is higher on $<1\bar{1}00>$ -offcut 5 epilayers of the present invention, doping control can be readily achieved using conventional techniques for such films. Figures 5 and 6 show doping control in 4H-SiC epilayers grown on substrates offcut $8^\circ \rightarrow <1\bar{1}00>$.

Figure 5 shows n-type doping control both by variation of input nitrogen partial pressure and 10 by site competition epitaxy (C/Si ratio variation) for 4H-SiC epilayers grown on substrates offcut 8° towards $<11\bar{2}0>$. The n-type doping density increases with increased input N_2 partial pressure as expected. The n-type doping density decreases with increasing C/Si, as expected by the "site competition" model developed by Larkin *et al.* (D. J. Larkin, P. G. Neudeck, J.A. Powell, and L. G. Matus, *Appl. Phys. Lett.* **65**, 1659 (1994)). P-type (Al) doping control via 15 TEA flow variation is also demonstrated in Figure 6 for films grown on (0001) 4H-SiC substrates offcut $8^\circ \rightarrow <1\bar{1}00>$.

Doping control within the epilayer was also demonstrated for 4H-SiC epilayers grown on substrates offcut $8^\circ \rightarrow <1\bar{1}00>$. Figure 7 shows the SIMS N profile of a 14 μm thick lightly 20 doped layer on a 1.5 μm undoped buffer (N detection limit is $2 \times 10^{16} \text{ cm}^{-3}$). The N level remains constant throughout the epilayer, and the undoped layer is clearly seen. The N doped region, the undoped region (ud) and the substrate (sub) are marked. The inset shows a SEM micrograph of the film cross section.

25 While we do not wish to be bound by a theory as regards the mechanism or basis of the improvement in doping character realized in the practice of the present invention, it is possible that the higher doping level in this offcut orientation may be explained by the surface bonding

configuration. Figure 8 shows the bonding configuration of the $<1\bar{1}00>$ surface. In previous work by Burk *et al.*, SiC epilayers were grown on on-axis $<11\bar{2}0>$ and $<1\bar{1}00>$ SiC substrates. The unintentional n-type doping was almost an order of magnitude higher on $<11\bar{2}0>$ orientation compared to the c-axis wafers, while the $<1\bar{1}00>$ epilayers contained 5 about two orders of magnitude higher doping than the $<11\bar{2}0>$ epilayers (10^{18} cm^{-3} range). They also noted a shift towards n-type doping for a-axis as compared to c-axis epilayers when intentional n- and p-type dopants were added. They were able to control the doping using site competition. In our own work we have used the more typical c-axis SiC substrate, and altered the offcut direction. Our unintentional n-type concentrations were $<2 \times 10^{16} \text{ cm}^{-3}$ (SIMS 10 detection limit). We were able to obtain n- and p-type doping control over five orders of magnitude when $<1\bar{1}00>$ -offcut substrates were used. Intentional n-type doping levels as low as $1 \times 10^{15} \text{ cm}^{-3}$ have also been achieved.

There are various advantages to growing SiC epilayers on substrates offcut toward the $<11\bar{2}0>$ 15 direction. Higher n-type doping levels can be achieved for 4H-SiC epilayers grown on substrates offcut $8^\circ \rightarrow <1\bar{1}00>$, compared to 4H-SiC epilayers grown on substrates offcut $8^\circ \rightarrow <11\bar{2}0>$, at the same gas ratio. The resultant higher doping concentrations on the 4H-SiC epilayers grown on substrates offcut $8^\circ \rightarrow <1\bar{1}00>$ lead to the formation of ohmic contacts with lower contact resistance. In epitaxial growth on 4H-SiC (0001) offcut toward $<11\bar{2}0>$, an 20 additional donor implantation step to reduce the contact resistance is required, and growth on the $<1\bar{1}00>$ orientation may eliminate the need for this additional step.

Lower contact resistances will improve the performance of a wide variety of devices. For example, the SiC MESFET frequency response will be improved by a reduction in contact- 25 induced parasitic series resistance. Higher n-type doping levels can be achieved using the doping parameters described herein, because of the increased doping efficiency of this orientation. The crystal quality is maintained, and the doping levels can be fully controlled,

when the $<1\bar{1}00>$ offcut direction is used. The unintentional impurity levels can also be kept sufficiently low to attain the desired doping levels.

The more uniform surface structure evident in Figure 5 also facilitates the removal of material

5 during device fabrication. The uniform structure increases the ability to accurately predict how much material is removed during etching, and the run-to-run and inter-wafer variation is reduced. Smooth and uniform etched surfaces improve the quality of the device passivation, the performance of etched Schottky contacts, and the overall device performance.

10 The more uniform, parallel-step surface structure on the $<1\bar{1}00>$ -offcut epitaxial surface facilitates high-quality oxide formation by reducing the density of interface trap states. The zig-zagged step structure found on SiC offcut towards the $<11\bar{2}0>$ will produce a higher dangling bond density per unit area than the parallel step structure. The step dangling bond density will be $\sim\sqrt{2}\times$ higher on surfaces miscut towards the $<11\bar{2}0>$ while the surface

15 dangling bond density will be equal for both. If the oxide interface defect density is taken to be proportional to the dangling bond density, the higher density of dangling bonds will lead to an oxide with a higher interface trap density. Further evidence for this advantage resides in the recent analysis of Lucovsky et al. (Applied Physics Letters 74(14), 2005 (1999)). In the ideal case of a dielectric on semiconductor, the average coordination number is three, a value that correlates with the formation of a very good or excellent oxide (a coordination number greater than three was determined to correlate with poor oxide formation). By adding steps, the coordination number increases at the step. Since the step edge density per unit area is greater on samples miscut towards the $<11\bar{2}0>$, this problem becomes worse, and the coordination number deviates further from the ideal.

20

Further, the nature of field emission sites below a deposited oxide will be different on surfaces grown on the $<11\bar{2}0>$ compared to the $<1\bar{1}00>$. The zig-zagged structure on $<11\bar{2}0>$

offcuts produces more deleterious point emitters, while the stepped structure on $<1\bar{1}00>$ offcuts produce more desirable edge emitters. Edge emitters emit at a higher field than a comparably high point emitter and consequently, the oxide deposited on the $<1\bar{1}00>$ miscut direction surface will require a higher electric field for breakdown. Increased step bunching, 5 even at low numbers of bilayers, e.g., 4 bilayers, may contribute to oxide breakdown. If the step bunching that has been observed on both miscut surfaces for very thick layers causes oxide breakdown, polishing can be effected more uniformly on the $<1\bar{1}00>$ surface.

Although the invention has been variously disclosed herein with reference to illustrative 10 embodiments and features, it will be appreciated that the embodiments and features described hereinabove are not intended to limit the invention, and that other variations, modifications and other embodiments will suggest themselves to those of ordinary skill in the art. The invention therefore is to be broadly construed, consistent with the claims hereafter set forth.

THE CLAIMS

5 What Is Claimed Is:

1. An epitaxial SiC film, grown on an offcut surface of a SiC substrate having a hexagonal crystal structure, with the offcut surface having an offcut angle of from about 6 to about 10 degrees, and the crystallographic direction of the offcut surface being towards one of the six equivalent $<1\bar{1}00>$ directions of the substrate \pm 7.5 degrees.
10
2. The epitaxial SiC film of claim 1, wherein the SiC substrate comprises 4H-SiC.
- 15 3. The epitaxial SiC film of claim 1, wherein the SiC substrate comprises 6H-SiC.
4. The epitaxial SiC film of claim 1, comprising a device quality SiC film.
5. The epitaxial SiC film of claim 1, wherein the offcut angle is from about 7 to about 9 degrees.
20
6. The epitaxial SiC film of claim 1, wherein the offcut angle is about 8 degrees.
7. The epitaxial SiC film of claim 1, wherein the offcut direction is towards one of the six equivalent $<1\bar{1}00>$ directions \pm 5 degrees.
25
8. The epitaxial SiC film of claim 1, wherein the offcut direction is towards one of the six equivalent $<1\bar{1}00>$ directions \pm 2.5 degrees.

9. The epitaxial SiC film of claim 1, wherein the offcut direction is towards one of the six equivalent $<1\bar{1}00>$ directions ± 1.5 degrees.
10. The epitaxial SiC film of claim 1, having a smooth surface morphology, within an edge exclusion area, characterized by a root mean square roughness not exceeding about 2 nanometers.
11. The epitaxial SiC film of claim 1, having a smooth surface morphology, within an edge exclusion area, characterized by a root mean square roughness of less than about 1 nanometer.
12. The epitaxial SiC film of claim 1, doped with an n-type and/or p-type dopant species.
13. The epitaxial SiC film of claim 1, doped with an n-type dopant species.
14. The epitaxial SiC film of claim 1, doped with a p-type dopant species.
15. The epitaxial SiC film of claim 1, doped with an n-type dopant species and a p-type dopant species.
16. The epitaxial SiC film of claim 1, doped with a dopant species at a dopant concentration of from about 1×10^{13} to about 1×10^{21} atoms $\cdot \text{cm}^{-3}$.
17. The epitaxial SiC film of claim 1, having a microelectronic device structure formed on or in the film.
18. A silicon carbide article, comprising:

a SiC substrate of hexagonal crystal form, with an offcut surface having an offcut angle of from about 6 to about 10 degrees, and the crystallographic direction of the offcut surface being towards one of the six equivalent $<1\bar{1}00>$ directions of the substrate \pm 7.5 degrees; and

5

an epitaxial SiC film, grown on the offcut surface.

19. The silicon carbide article of claim 18, wherein the SiC substrate comprises 4H-SiC.
- 10 20. The silicon carbide article of claim 18, wherein the SiC substrate comprises 6H-SiC.
21. The silicon carbide article of claim 18, wherein the epitaxial SiC film comprises a device quality epitaxial SiC film.
- 15 22. The silicon carbide article of claim 18, wherein the offcut angle is from about 7 to about 9 degrees.
23. The silicon carbide article of claim 18, wherein the offcut angle is about 8 degrees.
- 20 24. The silicon carbide article of claim 18, wherein the offcut direction is towards one of the six equivalent $<1\bar{1}00>$ directions \pm 5 degrees.
25. The silicon carbide article of claim 18, wherein the offcut direction is towards one of the six equivalent $<1\bar{1}00>$ directions \pm 2.5 degrees.
26. The silicon carbide article of claim 18, wherein the offcut direction is towards one of the six equivalent $<1\bar{1}00>$ directions \pm 1.5 degrees.

27. The silicon carbide article of claim 18, wherein the epitaxial SiC film has a smooth surface morphology, within an edge exclusion area, characterized by a root mean square roughness not exceeding about 2 nanometers.

5 28. The silicon carbide article of claim 18, wherein the epitaxial SiC film has a smooth surface morphology, within an edge exclusion area, characterized by a root mean square roughness of less than about 1 nanometer.

10 29. The silicon carbide article of claim 18, wherein the epitaxial SiC film is doped with an n-type and/or p-type dopant species.

30. The silicon carbide article of claim 18, wherein the epitaxial SiC film is doped with an n-type dopant species.

15 31. The silicon carbide article of claim 18, wherein the epitaxial SiC film is doped with a p-type dopant species.

32. The silicon carbide article of claim 18, wherein the epitaxial SiC film is doped with an n-type dopant species and a p-type dopant species.

20 33. The silicon carbide article of claim 18, wherein the epitaxial SiC film is doped with a dopant species at a dopant concentration of from about 1×10^{13} to about 1×10^{21} atoms cm^{-3} .

25 34. The silicon carbide article of claim 18, comprising a microelectronic device structure formed on or in the epitaxial SiC film.

35. A silicon carbide epitaxial material, grown on a (0001) 4H-SiC crystalline substrate

offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate.

36. The silicon carbide epitaxial material of claim 35, wherein the (0001) 4H-SiC

5 crystalline substrate has an offcut angle of from about 7 to about 9 degrees towards the

$<1\bar{1}00>$ crystalline direction of the substrate.

37. The silicon carbide epitaxial material of claim 35, wherein the (0001) 4H-SiC

crystalline substrate has an offcut angle of about 8 degrees towards the $<1\bar{1}00>$

10 crystalline direction of the substrate.

38. The silicon carbide epitaxial material of claim 35, doped with an n-type and/or a p-type

dopant species.

15 39. A 4H-SiC epilayer film grown on a (0001) 4H-SiC substrate offcut towards the

$<1\bar{1}00>$ crystalline direction of the substrate, wherein said epilayer film has a LEED

(0 $\bar{1}$) beam intensity profile substantially as shown in Figure 2.

40. A 4H-SiC epilayer film grown on a (0001) 4H-SiC substrate offcut towards the

20 $<1\bar{1}00>$ crystalline direction of the substrate, wherein said epilayer film has an

average root mean square roughness less than about 0.8 nanometers.

41. A silicon carbide article comprising a 4H-SiC epitaxial material on a (0001) 4H-SiC

single crystal substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the

25 substrate.

42. The silicon carbide article of claim 41, wherein the (0001) 4H-SiC single crystal substrate has an offcut angle of from about 7 to about 9 degrees towards the $<1\bar{1}00>$ crystalline direction of the substrate.

5 43. The silicon carbide article of claim 41, wherein the (0001) 4H-SiC single crystal substrate has an offcut angle of about 8 degrees towards the $<1\bar{1}00>$ crystalline direction of the substrate.

10 44. The silicon carbide article of claim 41, wherein the film is doped with an n-type and/or p-type dopant species.

45. A silicon carbide article comprising a 4H-SiC epilayer film grown on a (0001) 4H-SiC substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate, having a LEED (01) beam intensity profile substantially as shown in Figure 2.

15

46. A silicon carbide article comprising a 4H-SiC epilayer film grown on a (0001) 4H-SiC substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate, having an average root mean square roughness less than about 0.8 nanometers.

20 47. A method of forming a silicon carbide epitaxial film, comprising depositing said film on a silicon carbide substrate of hexagonal crystal form, offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate.

48. The method of claim 47, wherein the silicon carbide substrate comprises 4H-SiC.

25

49. The method of claim 47, wherein the silicon carbide substrate comprises 6H-SiC.

50. The method of claim 47, wherein the offcut angle is from about 7 to about 9 degrees.

51. The method of claim 47, wherein the offcut angle is about 8 degrees.

5

52. The method of claim 47, wherein the offcut direction is towards one of the six equivalent $<1\bar{1}00>$ directions ± 5 degrees.

53. The method of claim 47, wherein the offcut direction is towards one of the six equivalent $<1\bar{1}00>$ directions ± 2.5 degrees.

10 54. The method of claim 47, wherein the offcut direction is towards one of the six equivalent $<1\bar{1}00>$ directions ± 1.5 degrees.

15 55. The method of claim 47, further comprising doping the silicon carbide epitaxial film with an n-type and/or p-type dopant species.

56. The method of claim 55, wherein the silicon carbide epitaxial film is doped to a dopant concentration of from about 1×10^{13} to about 1×10^{21} atoms $\cdot \text{cm}^3$.

20

57. A method of forming a silicon carbide epitaxial film, comprising depositing said film on a (0001) 4H-SiC crystalline substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate.

25 58. The method of claim 57, wherein the (0001) 4H-SiC single crystal substrate has an offcut angle of from about 7 to about 9 degrees towards the $<1\bar{1}00>$ crystalline direction of the substrate.

59. The method of claim 57, wherein the (0001) 4H-SiC single crystal substrate has an offcut angle of about 8 degrees towards the $<1\bar{1}00>$ crystalline direction of the substrate.

5

60. The method of claim 57, wherein growth of said film is carried out at subatmospheric pressure conditions, using SiH₄ and CH₄ with a H₂ carrier gas as a gaseous source medium for said film deposition.

10 61. The method of claim 60, wherein growth of said film is carried out under growth conditions including temperature in the range of from about 1450 to about 1650°C.

62. The method of claim 60, wherein intentional in-situ doping of said film is carried out during growth of said film.

15

63. The method of claim 62, wherein doping is conducted with a dopant source for a dopant species selected from the group consisting of nitrogen, aluminum, phosphorus, boron, and vanadium.

20 64. The method of claim 62, wherein doping is conducted using N₂ gas to provide nitrogen as an n-type dopant of the film.

65. The method of claim 62, wherein doping is conducted using triethylaluminum to provide aluminum as a p-type dopant of the film.

25

66. The method of claim 57, including the step of fabricating an electronic device on the film.

67. A method of forming a silicon carbide epitaxial film, comprising growing said film on a (0001) 4H-SiC crystalline substrate offcut towards the $<1\bar{1}00>$ crystalline direction of the substrate, wherein said growing step comprises:

5 introducing a carrier gas, a vaporized silicon-containing material and a vaporized carbon-containing material into a growth chamber; and

10 maintaining the carrier gas, silicon-containing material and carbon-containing material flows and temperature condition for a time sufficient to grow a film of desired thickness.

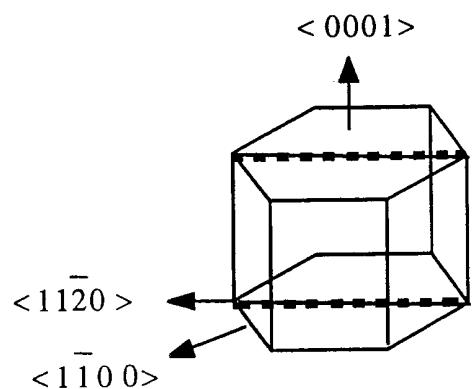


Figure 1

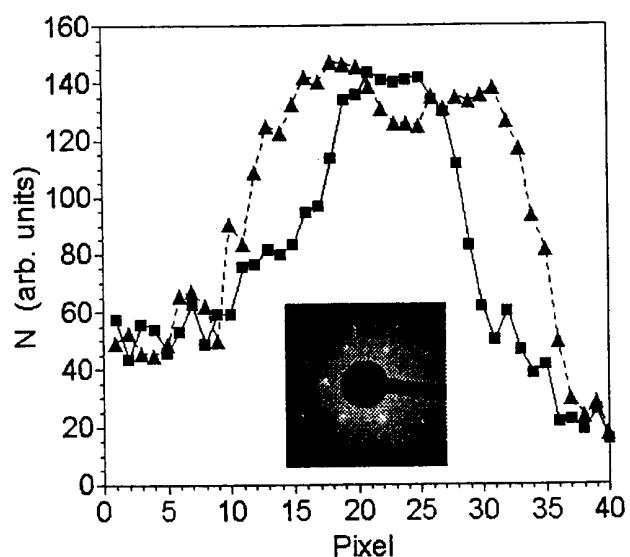


Figure 2

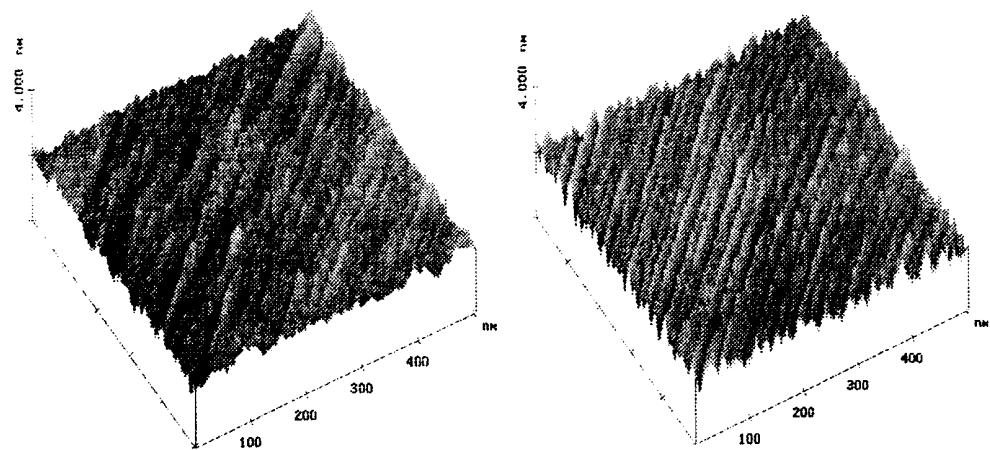


Figure 3

Figure 4

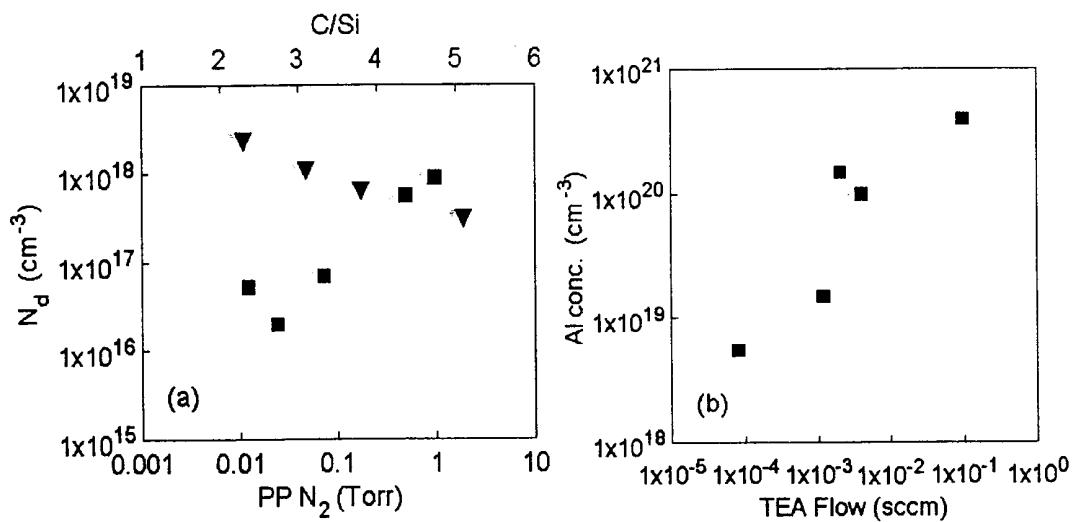


Figure 5

Figure 6

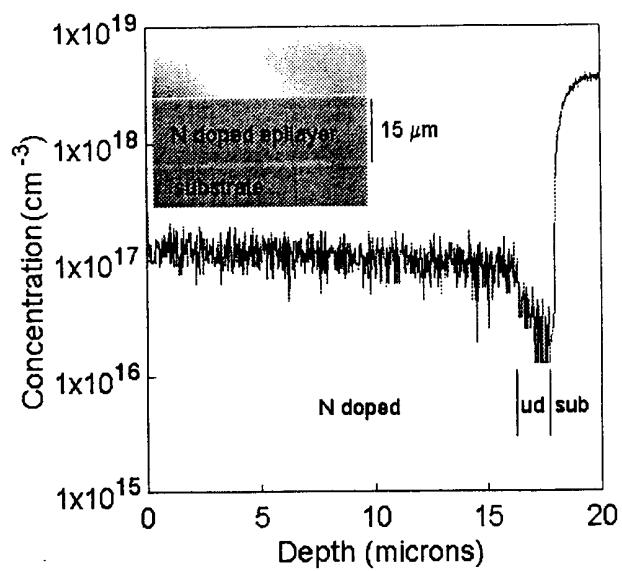


Figure 7

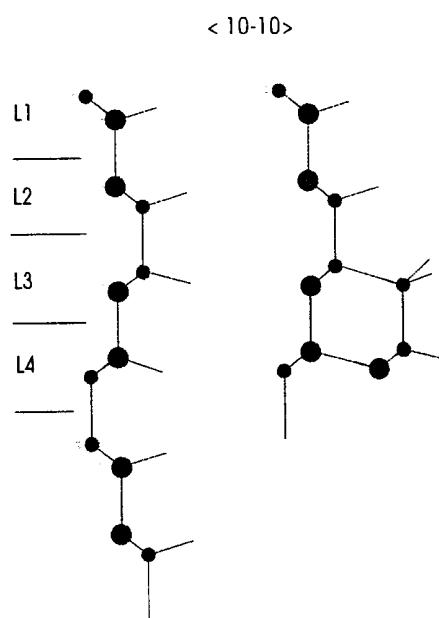


Figure 8