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Local control of SiC polytypes

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In the case of SiC different methods for the formation of laterally and vertically stacked desired polytype inclusions are presented. The methods are based on a combination of ion implantation and annealing combined with epitaxial growth by sublimation technique. Nanoheteropolytype structures were formed using CVD.

1 Introduction

Polytypism is a special one dimensional form of polymorphism and a general behavior of layered structures. The structural reason for this phenomenon is a low stacking fault energy and the possibility to form different modes of stacking of two dimensional structural compatible units along a definite direction [1, 2]. Physically the phenomena of polytypism and polymorphism are quite different from one to each other. The polymorphs of a material represent well defined thermodynamic phases, with specified stability ranges of temperature, composition and pressure. The transition of one polymorph to another is a first-order phase transformation. On contrary, except for a number of short period modifications, no such physical factors have been found to govern the formation of polytypes [3]. Different polytypes of a given material appear under identical conditions of temperature and pressure [4]. This lead to syntactic coalescence of polytypes and cause the formation of undesired microheterogeneous systems in the form of syntactical inclusions of different individual polytypes. The occurrence of such transitions was observed in practically every technologically relevant process, i.e. impurity diffusion and doping [5, 6], ion implantation and annealing [7, 8], sputtering [9], oxidation [10], metallisation [11] as well as crystal and epitaxial growth [12, 13] and during plastic deformation of single crystals [14]. Furthermore, especially in the case of high power devices, polytype transitions (PT) occur during the operation of semiconductor devices [15, 16]. Therefore, PTs are caused by energy dissipation. The dissipated energy is related to the thermodynamic fluxes and forces of the ongoing processes and can be described in the framework of nonequilibrium thermodynamics [4]. The energy dissipation and the relaxation processes lead to disorder formation in the polytype structures (PS). The disorder in this structures is strongly linked to the formation and propagation of stacking faults (SF) and partial dislocations (PD). The defect formation and propagation in turn is connected to the energy dissipation process [4, 17]. The local structural changes induced by the SFs are polytype inclusions, i.e. they introduce an element of a new PS. So, the energy

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dissipation in the crystal lead to an excess of structural information with respect to the PS. Collective and selective interactions between these defects result in a stability loss of the original structure [18]. Reaching the critical point non-equilibrium PT occur causing the formation of a new PS better adapted to the exterior conditions [4, 19].

The current paper will demonstrate local polytype selection and control by using: (1) sublimation growth technology in combination with ion implantation and (2) chemical vapour deposition (CVD) for the alteration of the substrate polytype. The developed techniques are complementary to the methods reported in [19].

2 Experimental

The epitaxial growth was carried out at 2100 K by the modified sublimation sandwich method in a quasi closed system [20]. As substrates 4H and 6H silicon carbide polytypes were used. For the surface and structural modification of the substrates, ion implantation of Al, Ar and N was carried out at room temperature at different acceleration voltages. The samples were investigated by reflection high energy diffraction (RHEED), plane view and cross sectional μ-Raman and in part by transmission electron microscopy (TEM). Only the nanoheteropolytype structures were grown by chemical vapour deposition at a base pressure of 10^{-9} mbar (UHVCVD technique) which is described in [21].

The plane view and cross sectional micro Raman spectroscopy (CS μ-RS) were carried out at room temperature utilizing a Dilor XY triple monochromator with a CCD camera as detector in the spectral range from 100 to 1000 cm^{-1} with an excitation wavelength of 501.7 nm (2.47 eV) of an Ar^+-laser and an incident power of 20 mW in crossed polarization configuration with the incident light polarized parallel to the $\langle 11\bar{2}0 \rangle$ direction. The penetration depth at the chosen wavelength is approximately 290 and 3200 μm for β-SiC and α-SiC, respectively. Cross-section scans were taken with a step width of 100 nm at a laser beam focus of about 1 μm. The evaluation procedure and the model for the simulation of the phonon peak intensity variations are described in more detail in [22, 23].

3 Results and discussion

In epitaxial growth the most critical step is the nucleation stage. In the case of the growth of polytype structures the surface conditions have to be chosen so that the epitaxial layer is able to replicate the underlying polytype structure. If lateral polytype patterning in the epitaxial layer is desired the surface or the nucleation and growth conditions have to be varied laterally. This can be done by surface step width adjustment [24, 25], supersaturation variation [5, 20, 25], surface defect formation [19] or tuning the silicon to carbon ratio [25–27]. From the technological point of view ion implantation is the most suitable method to alter laterally the growth condition.

3.1 Ion implantation and polytype structures

The dependence of the polytype structure on the implantation and annealing conditions were studied by implanting aluminium into 6H-SiC samples and annealing in Ar atmosphere and Si overpressure in a rapid graphite strip heater. The obtained results are summarized in Fig. 1a. As can be seen, if the implantation dose is kept below the dose necessary for surface amorphisation no polytype changes are detected on the surface by RHEED. At implantation doses above the surface amorphisation dose the annealing conditions can be tuned so that a change in the PS occurs at the surface. The PT is not only a function of the annealing temperature, but also depends on the heating up rate used during the annealing [28]. The heating rate and annealing temperature phase diagram is shown in Fig. 1b. According to Fig. 1a and b the polytype of the substrate can be retained if the following conditions are fulfilled: (1) the temperature during the annealing has to be high enough to prefer the nucleation and growth of α-SiC over β-SiC in the preamorphised layer, and (2) the residence time in the temperature region where the formation of β-SiC is preferred has to be negligible small.

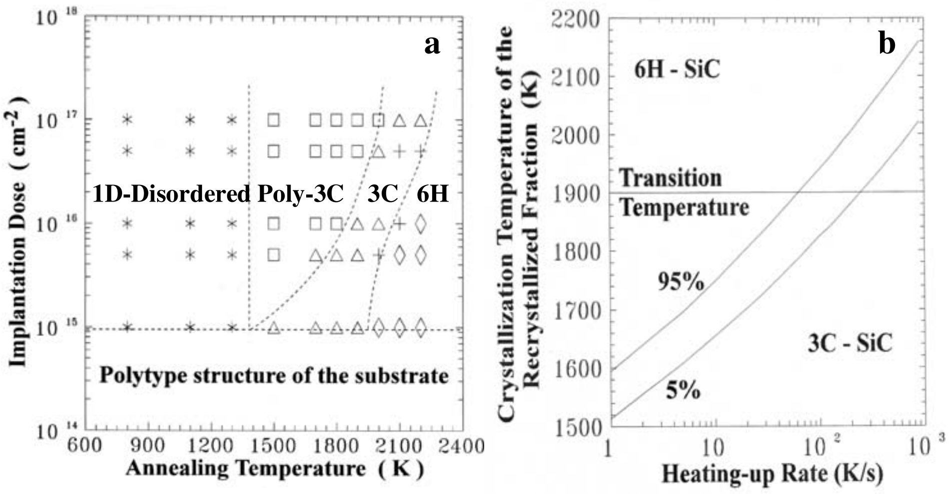

Fig. 1 (a) Al implantation dose – annealing temperature phase diagram for 6H-SiC (polytype structure of the substrate): * – one dimensional (1D) disordered SiC polytype, □ – polycrystalline 3C-SiC, △ – twinned 3C-SiC, + – polytype mixture of 3C and 6H, ◇ – 6H-SiC. The acceleration voltage was 80 keV. (b) Relationship between the occurrence of 3C-SiC and the heating up rate during annealing of the implanted layers. The ion implantation was carried out at room temperature.

3.2 Lateral patterning in epitaxial layers

The developed method of polytype patterning consists in the formation of desired polytype inclusions in the SiC substrate. To achieve this, standard steps of the planar technology were applied to a 6H-SiC $(000\bar{1})$C face substrate. The polytype prepatterning consists in a combination of ion implantation and annealing with subsequent epitaxial growth. The used process sequences are shown in Fig. 2a.

In a first step the SiC substrate was covered with a mask having window openings with a dimension of 50 by 50 μm^2. Through this mask the ion implantation was carried out. Ar$^+$ ions were implanted at an

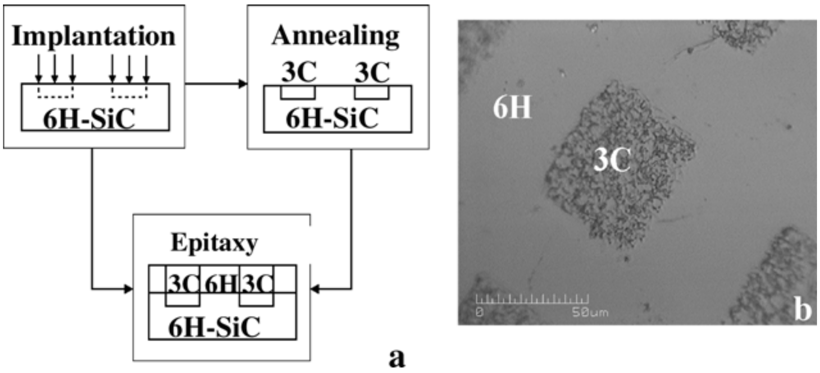

Fig. 2 (a) Schematical illustration of the possible process sequences to realise a lateral polytype patterned epitaxial layer using the formation of 3C-SiC in the implanted amorphised layer and the subsequent replication of the formed lateral polytype pattern during epitaxial growth. (b) Polytype 3C-SiC embedded in a 6H-SiC epitaxial layer on a $(000\bar{1})$C 6H-SiC substrate grown by modified sublimation sandwich method at 2100 K. The 3C-SiC prepatterning was carried out by implanting Ar$^+$ ions with a dose of 3×10^{15} cm^{-2} at 80 keV. The transformation of the amorphised regions into 3C-SiC in the substrate was realized during the heating up of the growth chamber to the deposition temperature.

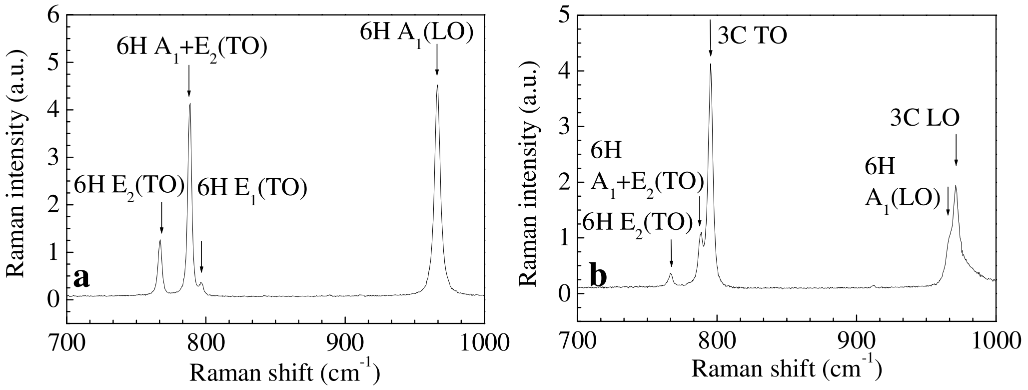

Fig. 3 Raman spectra taken from the 6H-SiC (a) and the 3C-SiC (b) areas in the epitaxial layer.

acceleration voltage of 80 keV and a dose of 3×10^{15} cm^{-2} at room temperature. Argon was chosen to avoid impurity effects during the subsequent epitaxial growth. At the chosen implantation conditions the implanted areas were completely amorphised. The following annealing procedure was designed in such a way that the implanted and preamorphised layers were completely transformed into 3C-SiC. This was proven by RHEED investigations monitoring the 3C-SiC diffraction spots at an azimuth of $\langle 11\bar{2}0\rangle$. Alternative to a single annealing step before carrying out the epitaxial growth an in situ PT process of the amorphised SiC regions into 3C-SiC was tested. The method consists in the integration of the recrystallisiation into the heating up phase of the epitaxial growth process. The heating up velocity was chosen in agreement with the data presented in Fig. 1b. The results of the PT process were checked by RHEED after interrupting the growth process before the nucleation sets in. As a result of the RHEED investigations 3C-SiC diffraction patterns were observed. The third process step consists in epitaxial growth by using sublimation epitaxy at 2100 K at a growth rate of 0.03 μm/s. The growth time was chosen to be 10 min. The growth conditions were designed so that the following requirements were fulfilled: (1) the different polytypes of the substrate were replicated by the epitaxial growth process, (2) the phase boundary between the areas of 3C-SiC and 6H-SiC were perpendicular and (3) no evolutionary selection between the both polytypes could occur. Such conditions for these two polytypes could be achieved when the growth conditions where close to the equilibrium growth condition. A typical result of the carried out experiments is shown in Fig. 2b where periodically arranged 50×50 μm^2 3C-SiC square embedded in a 6H-SiC layer are shown. In addition the PS of the different areas were investigated by μ-Raman spectroscopy. The results obtained are shown in Fig. 3a and b.

The spectra in Fig. 3a was taken from the areas in Fig. 2b labelled with 6H-SiC and indeed the recorded Raman spectra showed all the typical features for the 6H-SiC polytype [28]. Therefore, these regions consists of 6H-SiC. The Raman spectrum shown in Fig. 3b was recorded from areas labelled with 3C in Fig. 2b. This spectrum consists of an overlapping of strong 3C-SiC and weaker 6H-SiC features [28]. The weaker 6H-SiC peaks are due to the large penetration depth of the light used for the Raman scattering experiments, i.e. the 6H-SiC stems from the substrate.

3.3 Vertical polytype patterning

The formation of multilayer heteropolytype structures is one of most advanced challenges in fundamental research in SiC technology. To achieve a reproducible solution one task has to be solved at the beginning, the growth or formation of α-SiC on top of β-SiC. The data on such techniques to reach this goal is very scarce. Recently, the growth of α-SiC (4H and 6H) on top of β-SiC was achieved by carefully controlling the nucleation conditions during solid source molecular beam epitaxy of SiC [25] and during UHVCVD growth [27]. Here a technique based on ion implantation and epitaxial growth will be demon-

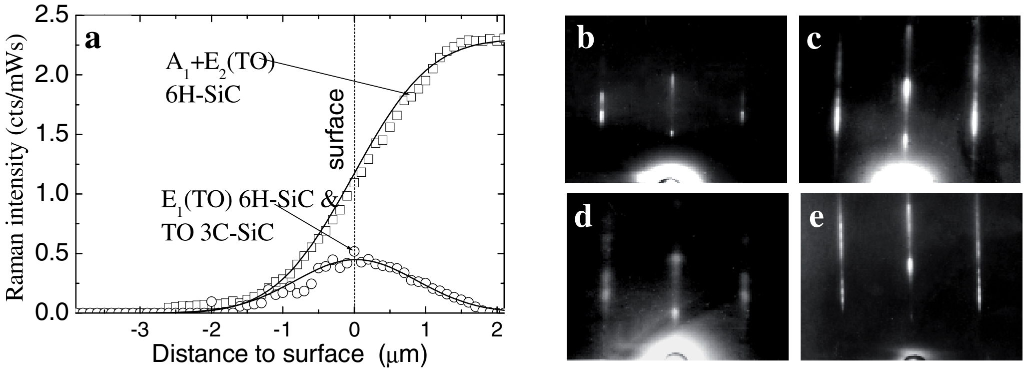

Fig. 4 Cross section μ-Raman scan of the 3C-6H-3C-6H heteropolytype structure (line – simulated, points – measurement) (a). RHEED pattern taken at different depths of the polytypic layer stacking: (b) 3C at the surface of the epitaxial layer, (c) 6H at 5 nm beneath the substrate surface, (d) 3C at 50 nm beneath the substrate surface, (e) 6H at 300 nm beneath the substrate surface. Azimuth: ⟨11$\bar{2}$0⟩.

strated which allows the multiple change of the polytype structure in layer stacks. The method is based on the described technique used in the case of lateral polytype patterning. The only difference is that the implantation conditions are chosen so that a buried 3C-SiC layer is formed after high temperature processing. Such 3C-SiC layers embedded in the bulk of 4H-SiC and 6H-SiC were intentionally created in a previous work [30].

The formation of the buried preamorphised region was realised by a double ion implantation of nitrogen with a dose of 3×10^{16} cm^{-2} at 30 keV and 3×10^{16} cm^{-2} at 80 keV. At this implantation condition the near surface area preserves its polytype structure. This region is approximately 5 nm thick. The preamorphised region is locate at a depth between 5 and 160 nm. The annealing of the sample was carried out during the epitaxial growth. The growth conditions were identical to the above described method except for the growth duration which was set to 1 min. The sample was investigated by cross section μ-Raman spectroscopy [22, 23]. The obtained spectrum is shown in Fig. 4a. The best fit of the phonon intensity variations versus scan distance was obtained by using a four layers model having the sequence 3C-6H-3C-6H (bulk material) with thicknesses 40/10/100 nm – 6H substrate. To confirm the Raman results a layer-by-layer investigation by RHEED was carried out. The crystal was etched step-by-step by anodic oxidation with subsequent etching in a HF solution. One etching step corresponds to approximately 5 nm. After every etching step a RHEED pattern was taken. The obtained results can be summarized as follows. The epitaxial layer consists of twinned 3C (Fig. 4b) followed by a approximately 10 nm thick 6H-SiC (Fig. 4c) located in the region near the surface of the substrate not preamorphised by the ion implantation. Beneath this thin 6H layer, a 110 nm thick twinned 3C-SiC region without inclusions of other polytypes was formed. The 3C-SiC layer is located in the region preamorphised by ion implantation (Fig. 4d). At larger depth the polytype of the substrate was formed (Fig. 4e). The thickness of the buried 3C-SiC is 55 nm smaller than the thickness of the preamorphised layer. The difference is caused by the inheritance of the polytypic structure at the amorphous-crystalline interface during recrystallization of the amorphous layer [31]. The change of the PS in the grown layer is due to the reduction of the critical growth rate leading to the 6H to 3C transition during epitaxial growth [19].

3.4 Towards nanohereropolytype structures

Generally all uncontrolled polytype transitions can be accounted as nanoheteropolytype structures, because the transition occur parallel to the basal planes in form of thin lamellas with sharp interfaces between the polytypes. The disadvantage of these structures is the lack of local control of their appearance. By using UHVCVD the formation of α-SiC on β-SiC/Si templates can be achieved [27]. The method

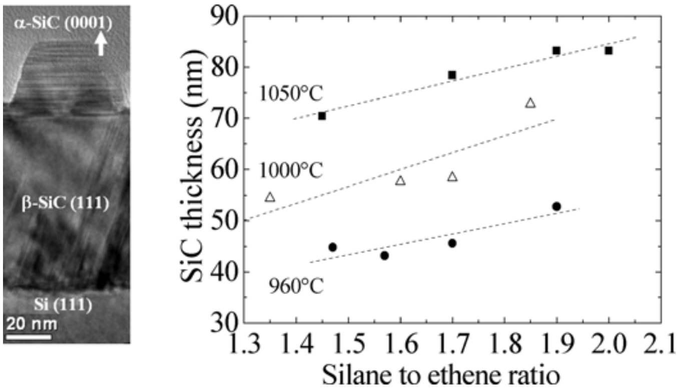

Fig. 5 (a) An α-SiC hillock grown on a 3C-SiC layer epitaxially grown on an Si(111) substrate. (b) 3C-SiC thickness versus growth conditions.

developed is based on the tuning of the Si to C ratio at the growing surface by taking into account the changing Si flux through the growing SiC layer. This lead to polytype transition from 3C-SiC to α-SiC and to the growth of a wide gap polytype on a polytype with a lower band gap (Fig. 5a) with an adjustable thickness (Fig. 5b).

4 Conclusion

Methods which allow local and reproducible changes of the polytype structure in bulk crystals and epitaxial layers are demonstrated for SiC. They are based on ion implantation and epitaxy as well as the ability of polytype crystals to reproduce their structure during processing. The developed methods introduce a new technological operation into the semiconductor technology – local polytype control.

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