α-SiC–β-SiC heteropolytype structures on Si (111)

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Nanoscale α-SiC(0001) on β-SiC(111) heterostructures on Si (111) substrates fabricated by ultralow-pressure chemical vapor deposition are demonstrated. The intentional formation of the α-β structure was achieved by adjusting the SiH_4 to C_2H_4 flux ratios to carbon rich conditions and by controlling the diffusion length. The developed method allows the formation of heteropolytypic structures with a controlled thickness of the intermediate cubic β-SiC layer. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2131179]

SiC is able to develop different stable stacking sequences along the direction perpendicular to the closed packed basal plane. This property is called polytypism. While the cubic variety of SiC (3C–SiC or β-SiC) presents a face-centered structure, the rest of the polytypes (α-SiC) develop hexagonal or rhombohedral arrangements. The most common α-SiC polytypes are 4H, 6H, 15R, and 21R. Since the band gap is the most interesting property in solid-state devices, SiC represents a family of semiconductor materials with the same stoichiometry but different band gaps. The exciton energy gap ranges from 2.4 eV for β-SiC (Ref. 1) to 3.4 eV for the pure hexagonal α-SiC polytype (2H–SiC).[2] This gives the opportunity to create new types of hetero- and low-dimensional structures using a combination of different polytypes. They exhibit identical chemical composition and would not suffer from chemical degradation, a common degradation effect in heterostructures and superlattices consisting of different materials. Furthermore, differences in the lattice constant in the basal plane are negligible small and can be adjusted by native defect concentration and doping. For these reasons, the intentional nucleation and growth of different polytypes on different substrates is of great interest. Moreover, the ability to integrate SiC nanoheteropolytypic structures on Si wafers becomes very favorable since the cheaper and well-developed Si technology can be exploited.

Another promising application field is the growth of hexagonal polytypes on foreign substrates, for example 4H–SiC on Si. Such an achievement would be advantageous, because structures with certain hexagonality exhibit different dislocation propagation directions than cubic Si due to their crystalline symmetry. This could contribute to the formation of large hexagonal seeds of great interest for large single crystal growth of SiC.[3] In the present investigations, a β to α-SiC transition occurring on Si substrates during epitaxial growth by chemical vapor deposition is reported. The process is based on the control of the temperature and the inputs of carbon and silicon precursors. The formation of hexagonal SiC polytypes on a cubic one was achieved up to now only by using molecular beam epitaxy,[4] a combination of sublimation and ion implantation,[5] or sublimation growth based technique at substrate temperatures around 2000 °C.[6,7]

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Radio Corporation of America procedure cleaned Si (111) wafers were loaded and transferred into an ultrahigh vacuum deposition chamber with a base pressure of 1×10^{-8} mbar. Mixtures of H_2, C_2H_4, and SiH_4 are used after a carbonisation step at flow rates of 10, 1, and 1–2.1 sccm, respectively. The substrate temperature was selected to be between 950 and 1120 °C with deposition times from 60 to 780 min. The used equipment and the growth procedure are described in more detail elsewhere.[8] Specimens for transmission electron microscopy (TEM) were prepared using mechanical thinning and Ar^+ milling in a Gatan precision ion polishing system. TEM and selected area electron diffraction (SAED) were performed in a TECNAI 20S-TWIN (FEI) microscope. The thickness was measured by reflectometry with a Mister WiT1000 equipment and confirmed by cross-section TEM (XTEM). Reflection high-energy electron diffraction (RHEED) investigations were carried out with a Staib EK35R system.

Figure 1 shows the polytype phase diagram determined as function of temperature versus precursors flux ratio. α-SiC appeared at SiH_4 to C_2H_4 flux ratios (R) ranging from 1.3 to 2 at temperatures between 950 and 1050 °C after 8 h of growth. The dotted line is just a guide for the eyes and delimitates the regions where α-SiC or β-SiC are formed at the surface of the epitaxial layer. Note that the incidence of stacking faults in SiC, event related with the first stages of α-SiC formation, were detected in RHEED patterns[9] (squares+circles in Fig. 1). The alpha SiC locates in this phase diagram in the region characterized by lower R values and lower substrate temperatures. An investigation of the surface and interface morphology reveals that the appearance

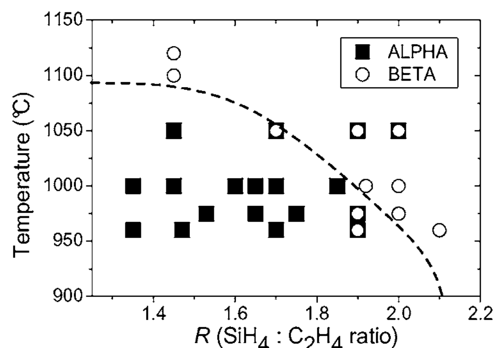

FIG. 1. Flux ratio-substrate temperature polytype phase diagram (■—α-SiC; ○—β-SiC; □—β-SiC with hexagonal stacking faults).

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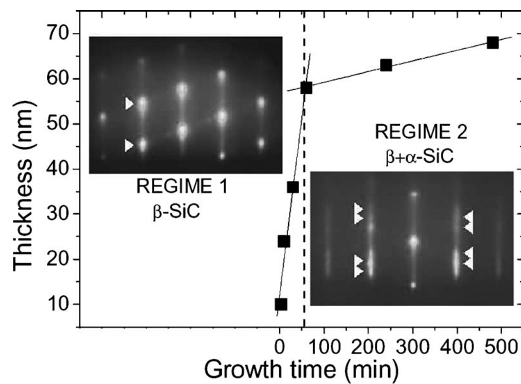

FIG. 2. SiC thickness with respect to the growth time for $R=1.35$. α-SiC was nucleated after a definite thickness of β-SiC of around 60 nm. Azimuths of RHEED patterns are $[1\bar{1}0]$ (left) and $[11\bar{2}0]$ (right).

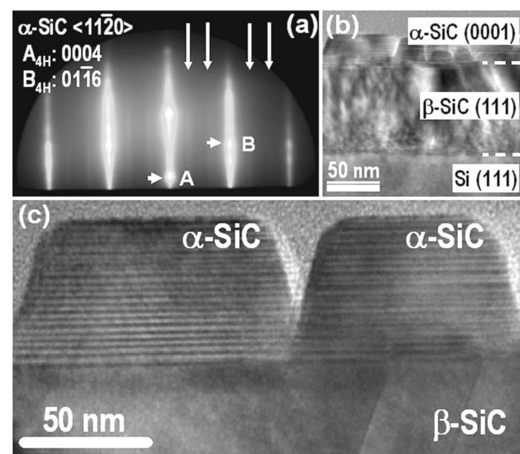

FIG. 3. RHEED pattern (Azimuth $[11\bar{2}0]$) (a) and TEM micrographs (b)–(c) of the sample grown at 1000 °C and $R=1.7$ for 13 h. Reflection spots (triangles) are indexed on the base of the 4H-SiC structure and surface reconstruction streaked lines are also visible (vertical arrows).

of the alpha phase is correlated with void formation at the SiC–Si interface. As an observed rule the density of the voids increases with decreasing R and increasing substrate temperatures. These features were not observed at $R \geqslant 1.9$. This observation indicates that the hexagonal polytype forms under conditions were the carbon supply limits the growth rate, i.e., carbon rich conditions.

Studies of the SiC growth kinetics and the correlated structural evolution in the epitaxial layer revealed a polytype transition during the epitaxial growth. A typical time dependent behavior is shown in Fig. 2 obtained in the case of 1.35 sccm of SiH_4 ($R=1.35$). α-SiC appears after a certain β-SiC thickness was formed. Therefore, two different time domains characterize the growth process. Every domain is characterized by the appearance of a different polytype at the surface (note the typical RHEED patterns in Fig. 2) and different growth rates. In the first time domain, β-SiC is formed (triangles point to SiC cubic reflections on the left RHEED pattern in Fig. 2). In the second time domain, i.e., after a definite β-SiC thickness, α-SiC nucleates and grows at the surface of the initially formed cubic SiC (left triangles pointing to 6H–SiC reflection spots in right RHEED pattern while the others are associated with 4H–SiC). Both polytypes are aligned along $[0001]_{SiC} \| [111]_{Si}$ and $[11\bar{2}0]_{SiC} \| [1\bar{1}0]_{Si}$ with respect to the Si (111) substrate. The growth rate is much faster in the first time domain than in the second one. Thus, when α-SiC starts to nucleate, the growth rate highly decreases.

TEM investigations were carried out to clarify the crystallography and the interface properties of the epitaxial heteropolytypic structure. Figure 3(a) shows the RHEED pattern collected along the $[1\bar{1}0]$ azimuth of the cubic substrate, corresponding to the sample grown at 1000 °C and $R=1.7$ for 13 h. Besides the vertical streaking and diffraction spots proper from α-SiC on the (01) and (0-1) rows, the vertical weak streaks at 1/3 and 2/3 of the fundamental position (vertical arrows) indicate a (3×3)-Si surface reconstruction evidencing the appearance of flat terraces on top of the α-SiC. This was confirmed by TEM investigations where a pyramidal shape was found for α-SiC islands [Fig. 3(c)]. The bright-field XTEM micrograph of Fig. 3(b) and corresponding SAED experiments also indicate the occurrence of an α-SiC (0001) layer formed by the coalescence of islands of similar height of around 20 nm after a thickness of β-SiC of 80 nm. The interface between the α- and β-SiC was found to be sharp and atomically abrupt. Furthermore, small regions of not complete or partial coalescence [Fig. 3(c)] of α-SiC nuclei with a height ranging from 15 to 30 nm were occasionally found along the wafer surface. Note that α-SiC islands present characteristic bright-dark contrasts related with the SiC polytype structure.[10] From the periodicity of these contrasts the polytype can be determined. At longer growth times, a coalescence of these nuclei forming flat and reconstructed surfaces was observed. The thickness of the β-SiC layer depends on the SiH_4 to C_2H_4 ratio and the substrate temperature. Therefore, a critical thickness can be determined for every growth condition. The dependence of the critical β-SiC thickness versus R with the substrate temperature as a parameter can be determined from Fig. 4. Note that the critical β-SiC thickness would be around 80% of the value of SiC thickness presented in the graphic as it was observed in selected XTEM preparations.

It was mentioned that the controlled nucleation and growth of different polytypes, especially on foreign substrates is a challenging task up to now. The most important factors influencing the appearance of different polytype structures during the epitaxial growth are: (1) the substrate temperature, (2) the supersaturation, (3) the surface diffusion, (4) the strain state, and (5) impurities. All these factors are coupled with each other in the growth process. In general it is accepted that polytypes growth stabilizes if the growth environment allows step flow growth, enabling the replication of the underlying substrate. A disturbance of this condi-

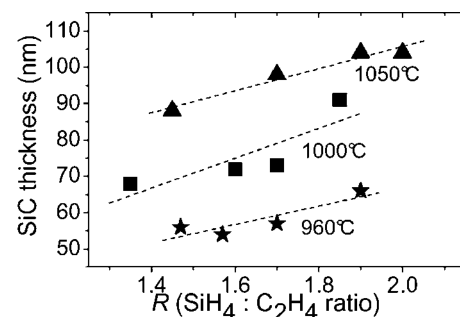

FIG. 4. β-SiC critical thickness vs R and temperature after 8 h of growth where the α-SiC islands have developed their maximum height. β-SiC thickness is around 80% of the presented $\alpha+\beta$ thickness.

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tion lead to two- or three-dimensional nucleation on surface terraces. In the case of the nucleation of a different polytype, a polytype transition in the epitaxial layer can occur. Therefore, for the stimulation of a desired polytpye transition during growth, two conditions have to be fulfilled. First, the new polytype has to be thermodynamically preferred over the initially formed and grown one. Second, the surface diffusion length has to be smaller than the terrace width to promote a nucleation on the terraces.

To analyze the appearance of the α-SiC on β-SiC the thermodynamic approach developed by Fissel[11] was applied. For the estimation of the carbon and silicon fluxes onto the surface, the partial pressure and the sticking coefficients shown by Annen *et al.*[12] were taken into account. The equilibrium partial pressures of the carbon containing species and silicon were determined by using the data of Avrov *et al.*[13] The pressure correction for the different polytypes and the strain effect were taken into account in agreement with Refs. 11 and 13. The supersaturation, S, is determined by the carbon flux onto the surface as $S=\xi \times P_{C_2H_4}/(P_{Si_2C}+P_{SiC_2})$, with ξ being the sticking coefficient and P_{Si_2C} and P_{SiC_2} the equilibrium species partial pressures. For the chosen growth conditions and a substrate temperature of 1000 °C a ratio between the formation energy in the case of two-dimensional nucleation, ΔG_2, and that of the three-dimensional nucleation, ΔG_3, was estimated. In the case of 4H–SiC the ratios were $\Delta G_2(4H)/\Delta G_2(3C)=0.81$ and $\Delta G_3(4H)/\Delta G_3(3C)=0.79$. This result supports the opinion that the hexagonal polytype is energetically preferred under the current growth conditions. Previous studies showed stabilization of α-SiC under C rich conditions.[11,14] At this point the question arises why the hexagonal polytype is not nucleated directly on the silicon surface. Three factors may lead to a preferred nucleation of the cubic polytype directly on the silicon surface. First, on the silicon surface carbon rich growth conditions cannot be achieved, due to the fact that the substrate directly contributes to the stoichiometry of the growth environment. This is supported by the increasing critical thickness of the 3C–SiC layer with increasing substrate temperature due to the increase of the Si out-diffusion through the β-SiC layer. Only if the Si supply from the substrate is negligible small compared to that of the growth environment, the gas phase plays the dominating role in the nucleation. The second factor is the high stress in the near interface region. The stress may lead to a stabilization of the cubic phase, because plastic deformation in hexagonal polytypes initiates a polytype transformation into 3C–SiC.[15,16] The final and the simplest argument is the replication of the underlying cubic substrate structure by the growing SiC.

The suppression of the α-SiC formation in the high temperature region at values of R above 1.9 can be explained by the surface diffusion on the SiC surface. As can be seen in Fig. 3 the terraces have a dimension of around 100 nm or larger. From previous studies[17,18] a surface diffusion length of 100 nm was extrapolated indicating on a preferred step flow growth at the used temperatures. Additionally, at these temperatures the Si diffusion through the growing SiC layer enhances leading to a shift of the surface conditions into a less carbon rich growth environment. If R is increasing, i.e., the growth conditions move towards silicon rich conditions, the diffusion length increases.[18] This also supports the step flow growth mechanism leading to a replication of the polytype structure of the underlying epitaxial layer and suppresses the nucleation of a new polytype structure.

In conclusion, the controlled nucleation and growth of alpha silicon carbide on a cubic silicon carbide Si (111) template has been demonstrated. The adjustment of the silane to ethene flux ratio and the substrate temperature allows to control the thickness of the underlying β-SiC layer.

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