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Structural characterization of ZnO nanopillars grown by atmospheric-pressure metalorganic chemical vapor deposition on vicinal 4H-SiC and SiO₂/Si substrates

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The structural characteristics of ZnO nanocrystals epitaxially grown on *p*-type (0001) 4H-SiC substrates were studied by transmission electron microscopy (TEM). The nanocrystallites were grown by atmospheric-pressure metalorganic chemical vapor deposition. The ZnO nanocrystals were formed at terraces introduced by vicinal 4H-SiC substrates toward the $[11\bar{2}0]$ direction. They had the shape of hexagonal nanopillars, with their edges parallel to the $\langle 11\bar{2}0 \rangle$ directions and a top *c*-plane facet, reflecting the crystal symmetry of ZnO. The free surface between the hexagonal nanopillars was covered by a very thin and highly defected epitaxial ZnO film, which strongly suggests the Stranski-Krastanov mode of growth. The ZnO/SiC interface was systematically studied by plane view TEM and cross sectional high resolution TEM. The residual strain in the thin continuous film as well as in the nanopillars was estimated from Moiré patterns and by geometrical phase analysis. ZnO was also deposited on the SiO₂/Si substrate for comparison. The films were polycrystalline exhibiting strong preferred orientation, with the *c*-axes of the grains almost perpendicular to the substrate resulting in the formation of nanopillars. The differences of nanopillar formation in the two substrates, 4H-SiC and SiO₂ is also discussed. © 2011 American Institute of Physics.

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I. INTRODUCTION

In terms of modern trends to decrease functional elements' size, the development of controllable deposition techniques of low-scale semiconductor materials is of great importance. ZnO as a prospective semiconductor allows us to obtain a number of meso- and nano-sized structures.^{1,2} The properties of ZnO depend closely on the microstructures of the materials, including crystal size, orientation, morphology, and aspect ratio.³ Nevertheless ZnO is a direct wide bandgap semiconductor with a high exciton binding energy (about 60 meV) exhibiting near UV emission and transparent conductivity that makes it promising for optoelectronic applications in the ultraviolet spectral region.^{1,4} Furthermore, ZnO is bio-safe and biocompatible, and may be used for biomedical applications without coating.⁵ Despite significant progress on ZnO nanostructures the difficulty in *p*-type doping of ZnO has impeded the realization of ZnO *p-n* junctions. An alternative approach may be the heteroepitaxial growth of ZnO on *p*-type semiconductors with the best candidate being GaN. However, in this case ZnO nanorods with a random distribution and mutual misorientation with the GaN substrate were obtained.⁶ An alternative approach is the heteroepitaxial growth on *p*-type 4H-SiC. Hexagonal SiC is attractive due to the 5.6% lattice misfit with ZnO in the basal

plane (expressed with respect to SiC), and the small thermal mismatch^{7,8} [thermal expansion coefficient (TEC) for 4H-SiC = $4.3 \times 10^{-6} \text{ K}^{-1}$], while ZnO is anisotropic: $\text{TEC}_a = 8.47 \times 10^{-6} \text{ }^\circ\text{C}$ (along the *a* axis of the hexagonal unit cell) and $\text{TEC}_c = 4.94 \times 10^{-6} \text{ }^\circ\text{C}$ (along the *c* axis).⁹

In this work the morphology and the growth mode of ordered low-sized ZnO nanocrystallites deposited by atmospheric-pressure metalorganic chemical vapor deposition (MOCVD) on a 4H-SiC *p*-type substrate were systematically studied. The high quality of these nanocrystallites explains the intense light emission in the ultraviolet spectral region.¹⁰ The present investigation is important due to the anomalies reported on the epitaxial growth of ZnO on 6H-SiC.¹¹ The ZnO nanopillars were also deposited on SiO₂/Si wafers, and the difference in the mode of growth of these nanocrystallites in comparison to the ZnO grown on SiC is discussed.

II. EXPERIMENT

For the growth of ordered low-sized ZnO structures on 4H-SiC, atmospheric pressure MOCVD (APMOCVD) was used, with the reactor geometry already described elsewhere.^{10,12} Zn acetylacetonates $[\text{Zn}(\text{AA})_2]$ and oxygen were used as precursors. Argon gas flow transported the vapor of the thermally decomposed Zn precursor to the reaction zone where due to mixing with oxygen, the ZnO deposits onto the substrate. For optimum growth conditions the 4H-SiC substrate temperature was kept at 500 °C and the flow rates of

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Ar buffer gas and oxygen were 50 and 25 sccm, respectively.¹² This enabled the growth of catalyst-free ZnO nanorods at relatively low temperatures (400–500 °C).^{13,14}

For the generation of nucleation centers, commercially available [0001] 4H-SiC substrates miscut by 8° toward the [11 $\bar{2}$ 0] direction were employed. Initially a *p*-SiC layer was epitaxially deposited on the 4H-SiC substrate by sublimation epitaxy,⁷ for the formation of a *p-n* heterojunction with the ZnO overgrown. The off-oriented substrate formation of surface steps along the [11 $\bar{2}$ 0] direction of the *p*-SiC is expected, as a consequence of the anisotropic growth rate and minimization of the surface energy in 4H-SiC.¹⁵ The bunched step height depends on the growth condition and in the present case was set close to 20 nm. These steps serve as nucleation centers for ZnO epitaxial growth. For the polycrystalline films the ZnO was deposited under the same conditions on 6 nm thick SiO₂ which was formed on (001) Si-wafers.

The microstructure and surface morphology were investigated by transmission electron microscopy (TEM), both plane-view TEM (PVTEM) and cross-sectional TEM (XTEM) observations were performed. For the conventional TEM characterizations a JEOL JEM 120 CX was used, while the high resolution TEM (HRTEM) analysis was performed using a JEOL JEM 3010 transmission electron microscope with point resolution of 0.17 nm. Scanning electron microscopy (SEM) was performed in a LEO 1550 Gemini SEM (at operating voltage ranging from 10–20 kV and a standard aperture value of 30 μ m). Quantitative strain measurements were performed on cross sectional HRTEM images by using geometrical phase analysis (GPA).^{16,17}

III. RESULTS AND DISCUSSION

A. ZnO nanocrystallites on 4H-SiC

The ZnO nanocrystallites exhibited the morphology of distorted hexagonal trapezoidal pyramids, as shown in the SEM micrograph in Fig. 1(a); the dark areas between the stripes correspond to 4H-SiC steps. The deposited ZnO nanocrystallites are shown in the low magnification XTEM micrograph in Fig. 1(b). The width of the nanocrystallites varied between 200–350 nm and their height ranged from 120–200 nm. In Fig. 1(b), individual crystallites are evident. The crystallites have a trapezoidal shape with flat planes on top. The angle between the flat planes on top of the trapezoidal crystallite and the SiC substrate was measured and found to be 7.635°, close to the nominal value of 8° of the miscut SiC substrate. This reveals that the growth of ZnO follows the *c*-axis of the miscut 4H-SiC. The nanocrystallites grew between adjacent steps of the substrate, as shown by the arrows in Fig. 1(b). The free surface of the 4H-SiC substrate between the hexagonal nanocrystallites was covered by a 2 nm thin layer, as shown at higher magnification in the inset in Fig. 1(b). The nature of this very thin layer was studied by PVTEM observations and will be discussed in the next paragraph. In some cases threading dislocation semiloops were observed, as indicated by an arrow in Fig. 1(c). The crystallites were in perfect epitaxial relation with the substrate having [0001]_{ZnO}//[0001]_{4H-SiC} and [10 $\bar{1}$ 0]_{ZnO}//[10 $\bar{1}$ 0]_{4H-SiC} as shown in the selected area diffraction (SAD) pattern of

FIG. 1. ZnO hexagonal nanopillars deposited on vicinal 4H-SiC substrate. (a) SEM image, and (b) XTEM micrograph of the deposited ZnO nanocrystallites. The arrows indicate that the top-plane of the ZnO hexagons is parallel to the SiC terraces. The space between the nanocrystallites is covered by a 2 nm thick film as shown in the inset. (c) A threading dislocation semiloop is shown by an arrow. (d) SAD pattern taken from the interface of a ZnO nanocrystallite with the 4H-SiC substrate.

Fig. 1(d). Due to the high misfit between ZnO and 4H-SiC in the basal plane (nominal 5.6%), the (10 $\bar{1}$ 0) reflections of ZnO and 4H-SiC are well-distinguished in Fig. 1(d). However the misfit along the *c*-axis between the (0002) and (0004) planes of ZnO and 4H-SiC, respectively, is only 3.5% and in this case the corresponding diffraction spots overlap.

The hexagonal ZnO nanocrystallites were also studied by PVTEM observations along the [0001] zone axis, as shown in Fig. 2(a). Well-developed hexagonal nanocrystallites with

FIG. 2. PVTEM micrographs of the nanocrystallites after thinning the specimen from the substrate side. (a) Hexagonal nanocrystallites at low magnification. The $[1\bar{1}20]$ edge of the hexagons points along the step flow direction. The free SiC surface between the nanocrystallites is covered by small patches denoted by arrows. (b) SAD pattern from the region of the nanocrystallite denoted by the letter A in (a).

their $[1\bar{1}20]$ edge pointing toward the step flow direction are evident. A SAD pattern obtained from the region of the nanocrystallite, denoted by the letter A in Fig. 2(a), is shown in Fig. 2(b). The well-aligned diffraction spots from ZnO and 4H-SiC confirm good epitaxial growth. The faint satellite spots around the main spots are due to double diffraction. The surface between the ZnO nanocrystallites was covered by a large number of small patches as indicated by arrows in Fig. 2(a). The high magnification PVTEM micrograph in Fig. 3(a) reveals that the space between the hexagonal nanocrystallites is covered by a thin ZnO film, as manifested by the presence of Moiré fringes produced by the interference of the electron beam with the superimposed 4H-SiC and ZnO lattices. A 2 nm thick film was already observed in Fig. 1(b); however it was too thin to give a diffraction pattern in XTEM. From Fig. 3(a) it can be seen that this thin film consisted of individual domains with an average size of 40 nm which are slightly misoriented, exhibiting a mosaic structure. Between the coalesced grains low-angle boundaries were formed as denoted by the arrows in Fig. 3(a). The grains were slightly misoriented, as is evident from the diffuse ZnO diffraction spots compared to the sharp 4H-SiC ones as shown in the inset in Fig. 3(a), and from the distortion of the Moiré fringes. The observed Moiré fringes in Fig. 3(a) are along the $[1\bar{1}00]$

FIG. 3. (a) PVTEM micrograph, taken under two near beam conditions, revealing that the space between the hexagonal nanocrystallites is covered by a very thin ZnO film manifested by the presence of Moiré fringes. Low-angle boundaries are indicated by arrows; the misorientation is evident by the distortion of the Moiré patterns. The corresponding diffraction pattern is shown in the inset. (b) Plan-view HRTEM micrograph taken with the electron beam parallel to the $[0001]$ direction. A net of Moiré fringes is evident. In the inset ZnO lattice planes are visible at higher magnification.

direction and were formed by the interference of the very strong $[1\bar{1}00]$ ZnO and SiC reflections, as shown in the inset of Fig. 3(a). Assuming that there is no rotation between the lattices, i.e., Moiré pattern of the translational type,¹⁸ the nominal fringe periodicity $D_{1\bar{1}00}$ is given by

$$D_{1\bar{1}00} = \frac{d_{\text{ZnO}} d_{\text{SiC}}}{d_{\text{ZnO}} - d_{\text{SiC}}} = \frac{d_{\text{ZnO}}}{\delta}, \quad (1)$$

where $d_{\text{SiC}} = 0.226$ nm and $d_{\text{ZnO}} = 0.281$ nm are the $(1\bar{1}00)$ interplanar spacings for 4H-SiC and ZnO, respectively, and δ is the nominal misfit expressed with respect to the substrate. Therefore, Eq. (1) gives a nominal periodicity $D_{1\bar{1}00} = 4.99$ nm for an unstrained epilayer lattice. The actual periodicity of the Moiré pattern measured in Fig. 3(a) is slightly larger than the nominal value for reasons we will discuss in the next paragraph. It is worth noting that the Moiré patterns are very sensitive, so that any local strain variation with respect to the matrix lattice results in significant distortion of the Moiré pattern. Hence the observed distortion of the Moiré patterns are attributed to local changes in the

epilayer lattice. According to Eq. (1) any lattice distortion is magnified in the Moiré pattern by a factor $1/\delta$. Also any rotation of the lattice of the epilayer with respect to the substrate by an angle Q is magnified by the factor $1/\delta$ according to the equation¹⁸

$$R = Q/\delta, \quad (2)$$

where Q is the actual misorientation of the crystal lattice and R is the observed rotational misorientation of the Moiré pattern. For example, in Fig. 3(a) the Moiré fringes between two adjacent domains are rotated by an angle $R = 13^\circ$. Therefore, according to Eq. (2), the real misorientation will be Q approximately 0.7° only, assuming the nominal misfit. In general the calculated misorientation of the ZnO domains in Fig. 3(a) did not exceed $\pm 1^\circ$. This explains the formation of low-angle boundaries and consequently the mosaic structure of the film. Thus, in our case any distortion of the overgrown lattice is magnified in the Moiré pattern by a factor of approximately 18. Therefore the Moiré pattern provides a simple direct method for the estimation of the residual elastic strain of the epitaxial film by comparing the observed with the nominal periodicity of Moiré fringes. For this purpose the periodicity of the Moiré fringes was measured in the high resolution PVTEM micrograph shown in Fig. 3(b), taken with the electron beam parallel to the [0001] direction. A net of Moiré fringes is evident and the mean value $D_{11\bar{2}0}$ of their periodicity along the three $\langle 11\bar{2}0 \rangle$ equivalent directions was deduced by measuring ten fringes in each direction and was found to be $D_{11\bar{2}0} = 3.692$ nm. Considering the SiC substrate to be undistorted and having the nominal spacing $d_{11\bar{2}0} = 0.15407$ nm, we have calculated from Eq. (1) the corresponding $D_{11\bar{2}0}^{zno}$ spacing for ZnO, which was 0.1608 nm. This value is significantly smaller than the nominal value 1.6267 nm, revealing that the ZnO film is under compressive strain. Due to this difference the residual misfit is 1.16%. The remaining 4.44% from the total 5.6% misfit is accommodated in a plastic manner by misfit dislocations at the ZnO/SiC interface and dislocations at the low-angle boundaries of the mosaic grains. In the inset of Fig. 3(b) the ZnO lattice in the section (0001) is shown at high magnification.

The three-dimensional (3D) island growth on a thin two-dimensional (2D) highly defected crystalline layer is a typical example of the Stranski-Krastanov mode of growth. Namely, after forming a few monolayers, the subsequent layer growth is unfavorable and islands are formed on top of this ‘intermediate’ layer.¹⁹ The residual strain in the ZnO nanopillars was estimated from cross sectional HRTEM observations.

Figure 4 illustrates a cross sectional HRTEM image of the interfacial region of a ZnO nanocrystal on SiC. It is seen that the interface comprises a bunched SiC step 9–13 nm in height. The uncertainty in the measurement of the step height results from the fact that the interface is amorphized at the ZnO side, as indicated at the right hand-side in Fig. 4. This is mainly due to the strain that is developed at the interface due to the lattice misfit, but the amorphization of the ion milling process also could contribute to this effect. The same effect has been observed during XTEM specimen preparation of 3C-SiC films epitaxially grown on Si.²⁰ In this

FIG. 4. Cross sectional HRTEM image of the ZnO/SiC interfacial region showing a bunched SiC step. On the right-hand side the interfacial structure is partially amorphized. A closed domain and an emanating threading dislocation in ZnO are indicated.

case the amorphous layer was formed at the interface in the Si side. The ZnO nanocrystal exhibits defects emanating from the interface. In particular, a closed domain comprising a local change of the defocus condition is quite visible, denoted by ‘dom’ in Fig. 4, which could possibly be attributed to polarity inversion. An emanating threading dislocation is also visible by faint contrast but it was made more discernible by the strain analysis as shown below. No detailed analysis of emanating defects was undertaken in this work as this was out of the scope of the present contribution.

Figure 5(a) is a Fourier-filtered image from the interface obtained from part of Fig. 4, which was taken with the electron beam parallel to the $[11\bar{2}0]$ direction. The Bragg image obtained from the interface by using the $1\bar{1}00$ spatial frequencies of ZnO and 4H-SiC is shown in Fig. 5(b), whereby extra half-plane planes in 4H-SiC are indicated. In this case 29 SiC lattice planes correspond to 28 ZnO planes. Considering the SiC substrate to be undistorted and taking the spacing $d_{11\bar{2}0}^{sic} = 0.2669$ nm we find the ZnO spacing $d_{11\bar{2}0}^{zno}$ equal to 0.2764 nm, significantly smaller of the nominal spacing 0.281776 nm revealing a residual compressive strain of 1.8% the remaining 3.8% misfit being absorbed by misfit dislocations. However, these measurements are not very accurate due to the large spacing between the misfit dislocations, large fluctuations in their periodicity, and interfacial amorphization, as shown in Fig. 4. For this reason a more accurate quantitative analysis was performed by using the GPA method.

The quantitative HRTEM (qHRTEM) analysis was performed by using the GPA method. Three distinct areas of the ZnO/SiC interfacial region were analyzed, starting from the edge of the nanocrystal and going toward the center. For each HRTEM image, 2D lattice strain maps were generated. For such mapping the substrate was assumed to be relaxed, exhibiting the nominal lattice constants $a_{SiC} = 0.3081$ nm

FIG. 5. Cross sectional HRTEM image along the $[11\bar{2}0]$ zone axis. (a) Fourier-filtered image from the interface. (b) Bragg-filtered image obtained by using only the $10\bar{1}0$ spatial frequencies. Misfit dislocations are evident at the interface.

and $c_{\text{SiC}} = 1.0053$ nm. The lattice strain maps were obtained by selecting the $g\ 1\bar{1}00_{\text{ZnO}}/1\bar{1}00_{\text{SiC}}$ and $g\ 0004_{\text{SiC}}/0002_{\text{ZnO}}$ spatial frequencies in the fast Fourier transform (FFT) of each HRTEM image, using Gaussian masks. Profiles of the variation of the lattice strain along $[0001]$ were then extracted for the two normal strain components $\epsilon_{xx}^{\text{lt}}$ and $\epsilon_{yy}^{\text{lt}}$, where the x -direction is $[1\bar{1}00]$, and the y -direction is $[0001]$ [i.e. $\epsilon_{xx}^{\text{lt}} = (d_{1\bar{1}00}^{\text{ZnO}} - d_{1\bar{1}00}^{\text{SiC}})/d_{1\bar{1}00}^{\text{SiC}}$ and $\epsilon_{yy}^{\text{lt}} = (d_{0002}^{\text{ZnO}} - d_{0004}^{\text{SiC}})/d_{0004}^{\text{SiC}}$]. The strain profiles extended for more than 20 nm in height into ZnO. The integration width for each profile along the $[1\bar{1}00]$ direction, over which the strain was averaged, ranged between 5–20 nm. In the following, strain measurements are discussed by illustrating maps obtained from one image, but average values from all three measured specimen areas are reported.

Figure 6(a) illustrates the map of the $\epsilon_{xx}^{\text{lt}}$ strain component obtained using a $g/5$ mask size (which corresponds to a spatial resolution of 1.3 nm). In order to enhance clarity, the map is shown superimposed on the HRTEM image. The map shows clearly that there is plastic relaxation of the strain by localization at the interface in the form of misfit dislocations [arrowed in Fig. 6(a)]. Figure 6(b) illustrates the $\epsilon_{xx}^{\text{lt}}$ strain

FIG. 6. (Color online) Map of the $\epsilon_{xx}^{\text{lt}}$ strain component, obtained using a $g/5$ mask size which corresponds to a spatial resolution of 1.3 nm. The map is shown superimposed on the HRTEM image. Arrows indicate localized interfacial strain fields corresponding to misfit dislocations. (b) Profile of $\epsilon_{xx}^{\text{lt}}$ along $[0001]$ obtained using the selection box indicated in (a). The width of the box along $[10\bar{1}0]$ is the employed integration width.

profile along $[0001]$ obtained from the selection box indicated in Fig. 6(a). It is evident from the profile in Fig. 6(b) that $\epsilon_{xx}^{\text{lt}}$ is less than the nominal value of the misfit $\delta = 5.60\%$. The lattice strain of ZnO along the growth direction was averaged, after discarding the measurements corresponding to the first 5 nm above the interface, where the profile is distorted due to defect emanation and interfacial amorphization. In a similar manner, strain measurements were collected from profiles in the rest two regions, and a total average from over 3000 measurements was extracted. This yielded $\epsilon_{xx}^{\text{lt}} = 4.10 \pm 0.30\%$, i.e. the lattice strain is 1.50% less than nominal. This corresponds to a residual compressive elastic strain in the basal plane of ZnO equal to $\epsilon^{\text{el}} = -1.42\%$. In Fig. 6(b) it is seen that as the thickness of the film increases, the lattice strain $\epsilon_{xx}^{\text{lt}}$ slightly increases having a tendency toward the nominal value, and hence the residual strain ϵ^{el} decreases somewhat. Even so the lattice strain is still much less than the nominal misfit.

Regarding the c lattice parameter, the average lattice strain, $\epsilon_{yy}^{\text{lt}}$, obtained from three images using a $g/5$ mask size around the $0004_{\text{SiC}}/0002_{\text{ZnO}}$, was $\epsilon_{yy}^{\text{lt}} = 3.61 \pm 0.44\%$, which is almost the nominal value of 3.67% between $c_{\text{SiC}}/2$ and c_{ZnO} (the nominal c lattice constant of ZnO is $c_{\text{ZnO}} = 0.52151$ nm). It is interesting to compare the measured value of $\epsilon_{yy}^{\text{lt}}$

with the predicted one if we assume a biaxial strain state introduced by the residual elastic strain on the basal plane (the so-called ‘tetragonal distortion’). In this case, the elastic strain along [0001] is given by the equation

$$\varepsilon_{yy}^{el} = -2 \frac{C_{13}}{C_{33}} \varepsilon_{xx}^{el}, \quad (3)$$

where C_{13} and C_{33} are elastic constants of ZnO. The employed values were $C_{13} = 118$ GPa and $C_{33} = 211$ GPa.²¹ The elastic strain is defined as $\varepsilon_{xx}^{el} = (d_{1100}^{ZnO} - d_{1100}^{relaxed-ZnO}) / d_{1100}^{relaxed-ZnO}$, and similarly for ε_{yy}^{el} . Eq. (3) yielded $\varepsilon_{yy}^{el} = 1.59\%$ from which we obtain a predicted value of ε_{yy}^{lt} equal to 5.40%. This is clearly much larger than both the experimentally measured ε_{yy}^{lt} and the nominal mismatch along the c -axis. Hence we conclude that despite the residual elastic strain in the basal plane, the strain state of the ZnO nanocrystals is not biaxial but closer to a plane strain condition. The strain along [0001] is probably relaxed by basal extra half planes that were observed to be inserted at the bunched substrate steps, but further work is required to clarify the exact mechanism.

The hexagonal nanocrystallites are two orders of magnitude thicker than the continuous film. Therefore, as the residual strain reduces with thickness, in the hexagonal nanocrystallites new misfit dislocations will be created. The new misfit dislocations are generated at the free surface and subsequently extend to the interface. Thanks to the relatively small width of the nanocrystallites the generated dislocations extend easily, rarely leaving threading segments in the interior of the crystallites, as shown in Fig. 1(c).

B. ZnO nanocrystallites grown on a SiO₂/Si substrate

ZnO nanocrystals were deposited on a SiO₂ layer about 5 nm thick, which was formed on a (100)-Si wafer. In this case massive nanopillar growth was observed, as shown in the SEM micrograph of Fig. 7. The crystallites had a conical shape, the average height from the top to the interface was about 110 nm, and the mean width was about 160 nm, as shown in the XTEM micrograph in Fig. 8(a). The nanopillars at the top of the nanocrystallites were not observed by XTEM for two reasons. Most of them were broken by pressing the two parts of the sample face-to-face for the XTEM

FIG. 7. SEM image showing nanopillar formation in polycrystalline ZnO.

FIG. 8. XTEM micrographs from the polycrystalline ZnO grown on SiO₂. (a) Conical grains are grown on a 5 nm thick oxide layer on the Si substrate. (b) Orientation of two individual crystallites. (c) PVTEM micrograph from the polycrystalline ZnO. The SAD pattern in the inset at the upper right corner taken from a large grain, shown by an arrow. The diffraction pattern in the inset at the lower left side of the figure was taken by the largest SAD aperture, which includes a large number of crystallites, diffraction rings are evident, and the (0002) ring is missing.

specimen preparation. Also during the ion milling process the nanopillars were worn out first, as they are the thinnest parts of the specimen. The conical crystallites exhibited a strong preferred orientation having the c -axis almost perpendicular to the substrate. This is shown in Fig. 8(b). The crystallite denoted by the letter A has the c -axis parallel to the

001 crystallographic direction of the Si wafer as the corresponding SAD pattern in the inset reveals. The grain denoted by the letter B, in Fig. 8(b) has the c -axis inclined to the substrate, as shown by the related SAD pattern in the left-hand side inset in Fig. 8(b). This crystal is not conical, having a flat top surface. The same morphology is observed in the adjacent crystallite C, which has also the c -axis inclined to the substrate.

The disadvantage of XTEM is the very limited field of observation, about three orders of magnitude lower than PVTEM. Therefore, the film was also studied by PVTEM observations in order to have an overall view of the morphology and the degree of preferred orientation of the ZnO crystallites. For this purpose the Si substrate was partially removed by thinning the specimen from the backside. Nanocrystallites with well-developed facets are shown in Fig. 8(c). When the crystallite size is comparable with the SAD

aperture, single crystalline spots corresponding to the (0001) section are observed, as shown by an arrow in Fig. 8(c). The polycrystalline nature of the film was evident when a larger SAD aperture was selected covering several nanocrystallites, as shown in the inset at the low left corner in Fig. 8(c). The strong preferred orientation is evident by indexing the diffraction rings in this figure. Thus, the rings (1 $\bar{1}$ 00), (1 $\bar{1}$ 01), (11 $\bar{2}$ 0) and (1 $\bar{1}$ 02) were identified. However, the (0002) ring, which should be lying between the (1 $\bar{1}$ 00) and (1 $\bar{1}$ 01) rings, was missing. This is due to the strong preferred orientation along the c -axis, because the (0002) lattice planes are almost perpendicular to the electron beam and consequently cannot satisfy the Bragg condition. The strong preferred orientation is an inherent property of the ZnO and is also observed in films deposited on SiO₂/Si wafers by magnetron sputtering at room temperature. In this case polycrystalline films with columnar grains exhibiting strong [0001] preferred orientation were formed, as shown in Fig. 9(a).²² Grains having the c -axis almost perpendicular to the 3 nm thick SiO₂ layer are evident in the SAD pattern shown in the inset of Fig. 9(a). The diffraction patterns of the polycrystalline ZnO were accurately indexed using the diffraction spots of the single crystalline (001) Si-wafer as a reference. The ZnO reflections are arcs instead of rings due to the strong preferred orientation. The preferred orientation is attributed to the very

FIG. 9. (a) XTEM micrograph exhibiting the columnar morphology of the film on SiO₂. The diffraction pattern from the Si-substrate and the overgrown ZnO are shown in the inset. (b) Cross sectional HRTEM image from the ZnO/SiO₂ interface revealing the early stage of growth. (c) Schematic representations of the crystallites during the early stage of growth at RT. For simplicity two extreme cases are considered; grains having their c -axes parallel or perpendicular to the substrate, respectively. (d) Nuclei having the c -axis perpendicular to the substrate grow faster than those having the c -axis parallel to the substrate.

FIG. 10. Cross sectional HRTEM image from a columnar grain exhibiting strong [0001] preferred orientation. The (0002) lattice planes are shown in the inset.

FIG. 11. Schematic representation of ZnO films on SiO₂ deposited at about 500 °C. For simplicity only grains having their *c*-axis parallel or perpendicular to the surface are illustrated. (a) The number of the stable nuclei, which are formed during the early stage of growth, do not cover completely the substrate. (b) Evolution of the grains and formation of nanopillars as the film grows.

anisotropic growth rates versus the crystallographic orientations, with the fastest one along the [0001] direction. Thus, during the early stage of growth a high number of small nuclei are formed covering the SiO₂ surface, as shown in the cross-sectional HRTEM image of Fig. 9(b). From these small nuclei only those having the *c*-axis almost perpendicular to the substrate survive. This is shown schematically in Fig. 9(c); for simplicity only nuclei having the *c*-axis perpendicular or parallel to the substrate are drawn. As the deposition proceeds nuclei having the *c*-axis perpendicular to the substrate grow faster, with overlapping grains having the *c*-axis almost parallel to the substrate, as schematically shown in Fig. 9(d). Due to the growth competition, columnar grains are developed as shown in the HRTEM micrograph of Fig. 10, which comprises coalesced grains. Lattice planes of (0002) type almost parallel to the substrate are shown in the inset. According to the nucleation theory at higher deposition temperatures, the critical nuclei are bigger in size and fewer in number as schematically shown in Fig. 11(a), not completely covering the substrate. As the deposition proceeds, grains having their *c*-axis parallel to the substrate will grow fast, laterally covering the substrate, while those having the *c*-axis perpendicular to the substrate will form nanopillars as shown in Fig. 11(b). This is the case already observed by SEM in Fig. 7. It is evident that the mechanism for the formation of ZnO nanopillars on SiO₂ is different from the one on SiC. In the former the nanopillar formation is attributed to the strong preferred orientation and to the growth-death competition mechanism. In the latter, the Stranski-Krastanov mode of growth is responsible. At first several ZnO monolayers are formed as soon as the surface adhesive force is stronger than adatom cohesive force. As the film grows, strain is accumulated due to the misfit and the adatom cohesive force becomes stronger than the surface adhesive force, leading to the formation of epitaxial three-dimensional islands.

IV. CONCLUSIONS

The structural characteristics of the ZnO nanocrystallites deposited on vicinal 4H-SiC substrates were studied. It was

shown that first a few monolayers of ZnO grow epitaxially on the 4H-SiC terraces on top of which high quality ZnO nano-hexagons evolve. Dislocations can move easily to the ZnO/SiC interface for misfit accommodation due to the small grain size. Conversely, ZnO films deposited under the same conditions on SiO₂/Si were polycrystalline exhibiting strong [0001] preferred orientation and nanopillar morphology. Both types of films exhibited a strong preferred orientation along the *c*-axis. However the mechanism for the formation of ZnO nanopillars on SiO₂ is different from this on SiC. In the former, the formation of the nanopillar is due to the strong preferred orientation and the growth - death competition mechanism. In the latter it is attributed to the Stranski-Krastanov mode of growth. In this mode several ZnO monolayers are formed as the surface adhesive force is stronger than the adatom cohesive force. As the film grows, strain is accumulated due to the misfit and the adatom cohesive force becomes stronger than the surface adhesive force. This leads to the formation of epitaxial three-dimensional islands.

The observed good quality of the ZnO nanocrystals on 4H-SiC explains the intense light emission in the ultraviolet spectrum.⁹ The high optical quality and the availability of *p-n* junctions of these nanopillars can be considered as a promising key element for nano-optoelectronics applications.

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