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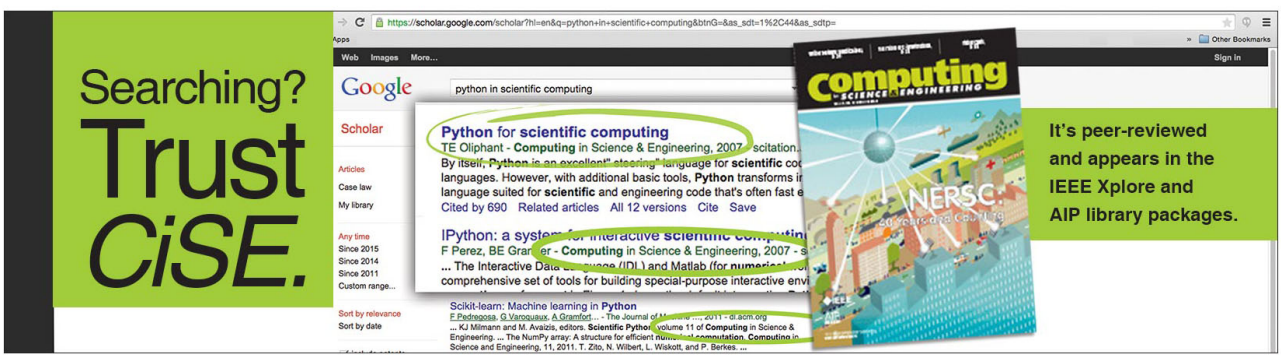

Selective growth of tilted ZnO nanoneedles and nanowires by PLD on patterned sapphire substrates

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We report the possibility to control the tilting of nanoneedles and nanowires by using structured sapphire substrates. The advantage of the reported strategy is to obtain well oriented growth along a single direction tilted with respect to the surface normal, whereas the growth in other directions is suppressed. In our particular case, the nanostructures are tilted with respect to the surface normal by an angle of 58°. Moreover, we demonstrate that variation of the nanostructures shape from nanoneedles to cylindrical nanowires by using SiO_2 layer is observed. [http://dx.doi.org/10.1063/1.4963076]

The piezoelectric properties and direct wide band gap make ZnO nanostructures, such as nanowires (NWs), promising building blocks for a variety of applications. The exploitation of ZnO NWs was already demonstrated e.g. for light emitters,[1] electromechanical resonators,[2] pressure and 3D imaging sensors[3,4] and energy harvesting.[5]

Beside NWs, also nanoneedles (NNs) are interesting, because they exhibit a sharp tip at one end. This offers a high sensitivity to electric fields and thus they can be used as probing tips for scanning probe microscope with high spatial resolution in both vertical and horizontal dimensions or field-emission tips due to the increased field-enhancement factor.[6] For the fabrication of these NWs and NNs the self organized growth of ZnO is typically leading to crystalline ZnO structures which are well oriented perpendicular to the surface.[7,8]

The optimum design, i.e. geometrical shape, orientation and density of the NWs and NNs depends on the desired functionality of the devices. For example, thick NWs with a thickness of several nm up to few μm are preferred for applications which are based on the strain and stress, e.g. caused by an externally applied pressure, thin NWs (few nm thick) offer a large surface-to-volume ratio, making them interesting for surface and bending sensitive applications.[9] Closely packed NWs with uniform spacing can improve light trapping and charge separation in nanowire-polymer solar cells.[10,11] By using tilted NWs and NNs, the field emission characteristic is controllable.[12,13] Additionally, tilted nanostructures can be used for the fabrication of asymmetric hyperbolic metamaterials.[14] Thus a high level of controll for the NW growth is desired especially to manipulate the growth direction.

The investigations of lateral NWs growth, i.e. NWs grown parallel to the surface plane, were presented in Ref. 3 and 15. Two approaches were developed for obtaining tilted NWs with respect to the surface normal. The first one involves using the self-tilting feature of NWs grown on *m*-plane sapphire without tilting of substrate itself and demonstrated by Zúñiga-Pérez *et al.*[16] The grown NWs are tilted with an angle of about ±30° with respect to the surface normal. The diameter, aspect ratio and crystal quality of such NWs are controllable. For several NWs applications unidirectional NWs are desired. Thus, the simultaneous growth of bidirectional by tilted NWs on one surface is undesired. Another approach, was presented by Yang *et al.*[10] which allows to grow locally unidirectional tilted

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NWs by using structured substrates. These substrates represent a periodic set of tilted Si facets made by wet-chemical etching. The Si(100) substrate is covered by a thin ZnO film. This thin film is used as seed layer for the NW growth and similar to a planar one the NWs grow parallel to the local surface normal of the thin film. Thus on these structures a high density NW growth is observed. However, the NW growth takes place on the whole sample and therefore, the growth of tilted as well as vertically aligned NWs obtained. Furthermore, also NWs tilted in the opposite directions are obtained which, in contrast to the approach mentioned in Ref. 16 are spatially separated. Therefore for manipulating the direction of the field emission or the formation of an hyberbolic media, these tilted NWs cannot be used. Here we show that by combining the two mentioned approaches, we can obtain NWs which are tilted in a single direction. We take advantage of self-organized growth of a dense, well oriented, high crystalline ZnO NWs on *a*- and *c*-plane sapphire as observed by several groups.[8,17] We used a structured *r*-plane oriented sapphire substrate containing only one tilted *c*-facet which support the growth of a high density NW array whereas, the other facets suppress the NWs growth.

The structured sapphire substrates were achieved by etching an *r*-plane sapphire substrate making use of the strong anisotropy of the etching rate following the different cristallographic planes. Thus, the etching process allows to obtain c-facets tilted with respect to the *r*-plane normal by an angle of about 58°. For fabrication of the structured sapphire substrate a 200 nm SiO_2 layer was sputtered on a *r*-plane sapphire wafer and etched in the form of stripes. The stripes have width of 7μm and a period of 10μm. In a second step the immersion in a 3:1 solution of H_3PO_4/H_2SO_4 at 270 °C during 20 min and subsequent rinsing in deionized water was performed. Owing to the much faster etching rate of the *c*-planes compared to the *r*-planes, the etching occurs preferentially in a lateral direction beneath the SiO_2 ridge. As a result, the final surface consists in about 8μm wide trenches and 2μm wide mesa covered with SiO_2. The depth of the trenches is around 400 nm. Due to the mentioned inhomogenous etching rate for the different sapphire facets a mesa structure with tilted *c*-facets is obtained. The preparation of these structures is explained in detail in Refs. 18 and 19. Four differently oriented surfaces for the further growth are present: *c*-facet, $\{1\bar{1}01\}$, SiO_2 on the mesa and the *r*-facet between the mesa. A scheme of the obtained structure is shown in Fig. 1. Only for the *c*-facet an oriented NWs growth is expected which would result in tilted structures. According to this, two situations may occur - on the one hand, the SiO_2 mask makes NWs growth difficult due to its non-crystalline structure.[20] On the other hand, removing the SiO_2 layer is leaves *r*-facet on the top of the mesa where no growth is expected. Thus, two types of substrates were prepared - one with and one without SiO_2 covering layer. For removing the SiO_2 layer an additional etching step was carried out, i.e. a wet-chemical etching in buffered HF solution for 15 min at room temperature was performed. Doing so, on the top of the mesa the *r*-facet is open.

The growth of the nanostructures is performed by high pressure pulsed laser deposition (PLD), with an oxygen partial pressure of p = 150 mbar with 50 sccm Ar and a growth temperature of T = 950 °C. A detailed description of the high-pressure PLD-chamber can be found in Ref. 21. The scanning electron microscope (SEM) images of the nanostructures obtained on patterned sapphire substrate with a SiO_2 layer on the top of the mesa are shown in Fig. 2. Here needle-like structures on both the SiO_2 layer and on the *c*-facet, are observable. On the *c*-plane oriented facet the NNs are well-oriented, with their *c*-axis perpendicular to this surface and therefore the NNs are tilted with respect to the substrate normal by 58° (Fig. 2a,b). Furthermore, the density of these NNs at this facet is quite high as it is well known for the growth of NWs on planar c-plane facets. In contrast, the NNs observed on the mesa covered with SiO_2 layer are not well oriented. For the *r*-plane oriented and $\{1\bar{1}01\}$ facets no growth of NWs or NNs was observed. The occurrence of the unwanted NNs on

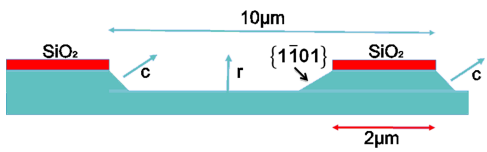

FIG. 1. Scheme of the structured sapphire substrates.

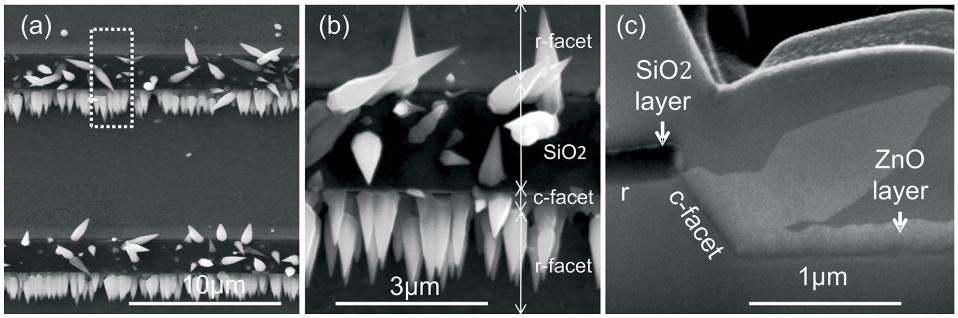

FIG. 2. The scanning electrone microscope (SEM) images of NNs obtained on the patterned sapphire substrate with SiO_2 mesa covering layer: (a) top view with low magnification, white dashed rectangle indicates area for high magnification and cross-section measurements, (b) top view with high magnification and (c) cross-section.

the SiO_2 layer can be a disadvantage for the tilted NNs application, hence the need to suppress the unwanted structures.

A cross-sectional SEM image of the obtained nanoneedles is shown in Fig 2c and reveals the complex shape of these structures. In the beginning of the growth, the nanoneedle broadens with increasing length so that it has a shape of an inverse pyramid which indicates that the growth in the lateral direction is preferred rather than along the axis of the NN. At a certain length of about 200nm in this case this behaviour changes. At this point, the growth along the *c*-axis becomes favored compared to growth in the radial direction with increasing length. Thus the diameter of the NN decreases with increasing length leading to a sharp tip at the end. The reason for this change in growth rate is not fully understood up to now.

We note that a similar behaviour was also observed for vertically grown NWs on planar surfaces.[8,22] At the beginning of the deposition only small number of ZnO particles leads to the growth of NWs with constant diameter along the NWs length. With increasing number of particles, i.e. with increasing NWs length, the diameter is changed along the NW.[22]

The growth of the NNs is accompanied by the growth of a thin ZnO layer and is observable on all facets. Interestingly, the thickness of this layer depends on the direction of the underlying facet. Whereas on SiO_2 the thickness of the ZnO layer is about 20 nm, the thickness on the *r*-plane facet is about 10 times larger, i.e. 200-250 nm. A reason for this difference can be that the ZnO particles which arrive from the plasma plume on the substrate might have a higher in-plane propagation length and thus can diffuse from the amorphous SiO_2layer to the crystalline *c*- and $1\bar{1}01$-sapphire facets. At *c*-facet, these particles contribute to the NN growth which might responsible for the asymmetric shape of the NN especially at the foot of the NNs.

We note, that the observed results do not depend on the orientation of the sample with respect to the plasma plume, i.e. if the *c*-facet is faced towards or opposite the plasma plume. This indicates, that the impact of the diffusion of the ZnO particles on the substrate is stronger for the growth of the nanostructures than the angle how the ZnO particles of plasma plume reach the substrate.

The results obtained for substrates with no SiO_2 layer on the top of the mesa are shown in Fig. 3. Similar to the substrates with a SiO_2 layer, a well oriented growth of nanostructures is observable for the *c*-facet. However, in this case we observe NWs instead of NNs. For the *r*-facet and the $\{1\bar{1}01\}$-facet some non-oriented NWs are observable, even between the mesa structures where no growth of nanostructures is expected based on the results discussed above. A reason for the different growth properties in this area might be caused by the additional etching step, used for this substrates in order to remove the SiO_2 layer. This might have changed some surface properties of the *r*-plane facet compared to the substrates which possessed the SiO_2 layer.

A cross-section SEM image of the tilted NW is shown in Fig. 3c and demonstrates the tilted growth of the NW wth respect to the substrate normal. Also the simultaneously growth of a thin ZnO layer, as discussed above, is observable. However in this case, the ZnO layer on and between the mesa is similar, around 5 – 10 nm. Since both surfaces are *r*-facets, it confirms the assumption

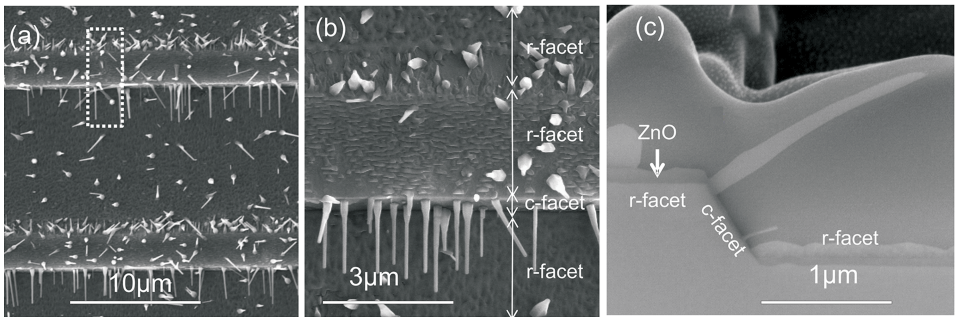

FIG. 3. The scanning electron microscope (SEM) images of the NWs growth results on patterned sapphire substrate without SiO_2 mesa covering layer: (a) top view with low magnification, white dashed rectangle indicates area for high magnification and cross-section measurements, (b) top view with high magnification, (c) cross-section.

mentioned above that the diffusion of the ZnO particles on the substrate strongly depends on the surface properties. Here the diffusion of the ZnO particles from the mesa towards the *c*-facet is reduced compared to those covered with SiO_2, which is reflected by the much larger thickness of the ZnO film, and thus the obtained NW is symmetric around the *c*-axis and much thinner than the NNs.

A detailed inspection of the NW shape also reveals a complex behaviour as obtained for the NN, i.e. a larger diameter of the bottom of the NW. This changes at a length of about 400 nm and a tapering of the NW is observable. Thus the same change in the preferred growth direction as observed for the NN is also present for the growth of the NW. However, this behaviour is much less pronounced than for the NNs, probably due to the fact that here the arrival of ZnO particles from the mesa part to the *c*-facet is much reduced.

In summary, we presented a strategy in order to achieve tilted nanowires and nanoneedles which are well oriented along one single direction by using structured substrates. We exploit the fact that the nanostructures grow predominantly on the *c*-facets of sapphire whereas the growth on the *r*-facets is suppressed. This allows us to select the spatial region of the substrate where the nanostructures grow. Furthermore, we demonstrate that we can switch between the growth of nanoneedles and nanowires by using an additional SiO_2 layer. The tilt of the nanostructures with respect to the surface plane of the substrate, is determined by the tilt of the *c*-facet and we suggest that also other angles are possible for patterned corrugated substrates.

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