

Biaxially Textured Titanium Thin Films by Oblique Angle **Deposition: Conditions and Growth Mechanisms**

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Growing highly crystalline nanowires over large substrate areas remains an ambiguous task nowadays. Herein, a time-efficient and easy-to-handle bottomup approach is demonstrated that enables the self-assembled growth of biaxially textured Ti thin films composed of single-crystalline nanowires in a singledeposition step. Ti thin films are deposited under highly oblique incidence angles by electron beam evaporation on amorphous substrates. Substrate temperature, angle of the incoming particle flux, and working pressure are varied to optimize the crystallinity in those films. Height-resolved structure information of individual nanowires is provided by a transmission electron microscopy (TEM) nanobeam, high-resolution TEM, and electron diffraction. Ti nanowires are polycrystalline at 77 K, whereas for ≥300 K, single-crystalline nanowires are tendentially found. The Ti crystals grow along the thermodynamically favored c-direction, but the nanowires' tilt angle is determined by shadowing. Biaxially textured Ti thin films require a certain temperature range combined with highly oblique deposition angles, which is proved by X-ray in-plane pole figures. A general correlation between average activation energy for surface self-diffusion and melting point of metals is given to estimate the significant influence of surface self-diffusion on the evolution of obliquely deposited metal thin films.

1. Introduction

Tailoring the texture of nanostructured thin films has been in the focus of manifold research activities in the last decades,^[1,2] and some promising applications for such films can already be deduced.^[3–5] In addition to representing a powerful technique to create thin films composed of 3D separated nanowires, oblique angle deposition (OAD)^[6-8] bears the potential to tailor the

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DOI: 10.1002/pssa.201900636

texture of these films.^[9–12] The characteristic of OAD is that the substrate is tilted to a highly oblique incidence angle θ_{OAD} with respect to the particle flux direction. Among the various techniques that can be used to deposit thin films by OAD, evaporation is the most widely used physical vapor deposition method, because there are rare interparticle collisions and consequently linear trajectories even at long distances between particle source and sample surface. This results in a highly linear, collimated vapor flux favoring ballistic shadowing, which is of major importance for OAD. During growth, the developing nanowires cast shadows, where later arriving particles cannot condense. As the growth process proceeds, the nanowires with a faster vertical growth component will shadow those with slower vertical growth.^[13] As different crystal planes of the same crystal grow with different rates. a selection of crystal orientations takes place during the competitive growth process. Thereby, the distribution of crystal orientations and accordingly the texture

of the nanowire thin film is changed. Fiber texture means that the crystals in the thin film share one mutual preferred growth direction in the polar direction, whereas an additional confinement of the crystal orientations in azimuthal direction defines a biaxial texture. In previous studies,^[14,15] we have already shown that the texture of nanowire Ti thin films deposited by electron beam evaporation at room temperature (RT) changes from fiber texture to biaxial texture as the deposition geometry becomes more oblique. These biaxially textured thin films were composed of separated nanowires that tend to grow as single crystallines. In the present study, the analysis of texture formation of these films is extended in terms of the influence of the substrate temperature. The structure of individual Ti nanowires is studied at different substrate temperatures as well. Additionally, the tilt angle of the *c*-axis of the hexagonal close-packed (hcp) Ti crystals with respect to the incoming particle flux is examined for varying incidence angles and substrate temperatures. An explanation is provided as to why the nanowires' tilt angle is not equal to the tilt angle of the Ti crystals' c-axis. Based on an empirical observation, an estimation is derived that allows to quantitatively estimate the surface self-diffusion length of an adatom.

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2. Results and Discussion

2.1. Structural Analysis of Individual Ti Nanowires

Nanowire Ti thin films are fabricated using a highly oblique angle of the incoming particle flux, $\theta_{OAD} = 82^{\circ}$, with respect to the substrate normal. The substrate temperatures are varied between 77 K \leq $T_{\rm Sub} \leq$ 873 K (0.04 \leq $T_{\rm H} \leq$ 0.45). $T_{\rm H}$ denotes the homologous temperature, which is calculated by normalizing the actual substrate temperature to the melting point of the material, T_{Melt} : $T_{\text{H}} = T_{\text{Sub}}/T_{\text{Melt}}$ (both in K). The top-view and corresponding cross-sectional scanning electron microscopy (SEM) images are shown in Figure 1. These images confirm that the Ti thin films are composed of individual nanowires that are inclined toward the incident particle flux, but the nanowires' tilt angle β as well as the nanowires' diameter *d* change significantly as the substrate temperature is varied from 77 K ($d \approx 50$ nm) to 873 K ($d \approx 350$ nm). Notice that with increasing substrate temperature, the high-aspect-ratio nanowires transform to columns with lower aspect ratios. Therefore, in the following, the structures obtained at 77 and 485 K are noted as nanowires, whereas for higher temperatures, those structures are named as columns.



Exemplarily for the nanowire Ti thin film grown at 77 K, the structure of individual Ti nanowires is analyzed by nanobeam electron diffraction (NBED). For this purpose, the electron beam is carried along the individual nanowire, starting from the substrate up to the top-most part of the nanowire. **Figure 2** and **3** are bright-field overview transmission electron microscopy (TEM) images of such a thin film. A selection of the resulting NBED patterns is shown in Figure 2 (I–IV) and Figure 3 (V–VIII). Distinct spots are detected in all NBED patterns, thus indicating a polycrystalline structure. The electron diffraction patterns in Figure 2 (II) and Figure 3 (VI) can be identified with those diffraction patterns as expected for a hcp Ti single crystal. For both patterns, the zone axis is Ti[111].

The high-resolution TEM (HRTEM) overview image in **Figure 4** includes details of two Ti nanowires from Figure 3. A crystalline structure of the nanowires is obtained, but the crystals in the nanowire have different orientations as the magnified HRTEM images in Figure 4 (I, IV) indicate. A closer inspection of the HRTEM overview image shows that each nanowire is surrounded by a TiO_x layer (see Figure 4 (III)), which is formed naturally as the sample is removed from the ultra-high vacuum (UHV) deposition chamber. These TiO_x layers exhibit crystalline



Figure 1. Top-view and corresponding cross-sectional SEM images of Ti thin films grown with an oblique angle of incidence $\theta_{OAD} = 82^{\circ}$ and with substrate temperatures varying between 77 and 873 K. The white arrows indicate the direction of the incoming particle flux. The tilt angle is β and the diameter is denoted by *d*. The angle of the incoming particle flux is θ_{OAD} .



Figure 2. Bright-field TEM overview image for Ti nanowires grown at $T_{Sub} = 77$ K (the homologous temperature $T_H = 0.04$) on thermally oxidized Si(100) substrates at $\theta_{OAD} = 82^\circ$. (I–IV) Corresponding NBED patterns. The zone axis in (II) is Ti[111].







Figure 3. Bright-field TEM overview image for Ti nanowires grown at $T_{Sub} = 77$ K ($T_H = 0.04$) on thermally oxidized Si(100) substrates at $\theta_{OAD} = 82^{\circ}$ (I–IV). Corresponding NBED patterns. The zone axis in (VI) is Ti[111].



Figure 4. a) HRTEM overview image of Ti nanowires grown at 77 K ($T_{\rm H} = 0.04$) on a thermally oxidized Si(100) substrate at $\theta_{\rm OAD} = 82^{\circ}$ (I–V). Magnified HRTEM images.

as well as amorphous regions. Further, partly amorphous regions are obtained between the TiO_x layers of two neighboring Ti nanowires, as shown in Figure 4 (II, V). These regions are expected to originate from the platinum that has been deposited on the sample during the preparation of the focused ion beam (FIB) lamella.^[16] It can be noted that highly oblique deposition at 77 K substrate temperature results in the formation of polycrystalline Ti nanowires. Previously, it was reported^[14,15] that single-crystalline Ti nanowires are formed if the deposition is conducted at RT (see **Figure 5**).

For comparison, tilted Ti columns are deposited obliquely $(\theta_{OAD} = 84^{\circ})$ at $T_{Sub} = 679$ K ($T_{H} = 0.35$). Figure 6a shows a bright-field TEM overview image of an agglomeration of such smaller and larger Ti columns. This agglomeration originates from scratching the TEM grid over the sample to collect those columns. The distinct spots in the diffraction patterns of the larger columns in Figure 6b,c show the presence of large crystals, which is an indication for the tendency of the single-crystalline growth of the individual Ti columns. The zone axes are determined to be Ti[201] for Figure 6b and Ti[120] for Figure 6c. The different zone axes are due to the random distribution of



Figure 5. HRTEM image of the detail of a Ti nanowire grown at RT ($T_{\rm H} = 0.15$) with $\theta_{\rm OAD} = 84^{\circ}$. The oxide layer is formed naturally as the sample is removed from the UHV chamber.

the columns on the TEM grid. To sum up, deposition at 77 K ($T_{\rm H} = 0.04$) results in the formation of polycrystalline Ti nanowires, whereas for deposition at $T_{\rm Sub} \ge 300$ K ($T_{\rm H} \ge 0.15$), the tendency for single-crystalline growth is observed.

As already indicated in a previous study,^[14] the observation that Ti nanowires grow as single crystallines at RT is in contrast to findings by Sadeghi-Khosravieh and Robbie,^[17] who reported on the growth of polycrystalline Ti nanowires under similar experimental conditions. However, in that study,^[17] the deposition was conducted at a working pressure of $p_{\text{Work}} \approx 10^{-4} \text{ Pa}$ (base pressure $p_{\text{Base}} \approx 10^{-5} \text{ Pa}$), but the Ti nanowires in the present study are grown at $p_{
m Work} \approx 1 \times 10^{-6}$ Pa ($p_{
m Base} \approx 10^{-6}$ Pa). The following experiments are conducted to examine the influence of the working pressure on the formation of the nanowires' structure. First, nanowire Ti thin films are fabricated by oblique deposition at $\theta_{\text{OAD}} = 88^{\circ}$ at $p_{\text{Work}} \approx 1 \times 10^{-6}$ Pa. Second, nanowire Ti thin films are grown with similar deposition parameters, but 0.3 sccm air flow from the environment is inserted into the chamber during deposition, resulting in an increased working pressure, $p_{\rm Work} \approx 2 \times 10^{-5}$ Pa ($p_{\rm Base} \approx 3 \times 10^{-4}$ Pa). The environmental air is allowed to flow directly to the substrate. Figure 7a,b shows the top-view SEM images of the

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Figure 6. a) Bright-field TEM overview image of an agglomeration of Ti columns deposited with $\theta_{OAD} = 84^{\circ}$ on a thermally oxidized Si(100) substrate at 679 K substrate temperature ($T_{H} = 0.35$). b,c) Corresponding SAED patterns. The zone axes are Ti[201] for (b) and Ti[120] for (c).



Figure 7. Top-view SEM images of tilted Ti nanowires deposited at $\theta_{OAD} = 88^{\circ}$ at RT on thermally oxidized Si(100) substrates with a) $p_{Work} \approx 1 \times 10^{-6}$ Pa and b) $p_{Work} \approx 2 \times 10^{-5}$ Pa (higher pressure realized by inserting 0.3 sccm air flow from environment during deposition).

corresponding nanowire Ti thin films grown without and with air, respectively. In contrast to Figure 7a, in Figure 7b, several branches on the nanowire surface are shown. These branches do not necessarily exhibit the same orientation as the primary crystal. Obviously, the formation of branches can be attributed to the presence of air during deposition, but it has to be clarified which component of the air causes the growth of those branches. An explanation for the formation of branches has been provided by Wang et al.,^[18] who reported about branched nanowires for vertical Cu nanowires deposited obliquely by magnetron sputter deposition. A grain boundary at the interface between the branches evolves so that it is energetically less favorable for later arriving particles to condense on the absorption site provided by the grain boundary. This results in a spatial separation of the branches, which is further deepened by the extreme shadowing as induced by the highly oblique deposition geometry. Molecular dynamic simulations by these authors^[18] confirm this mechanism.

To draw a conclusion, the formation of unbranched single-crystalline nanowires by OAD at RT requires, first, a sufficiently low pressure during deposition. Second, the adatom mobility has to be large enough to allow the formation of single-crystalline nuclei. Third, an adequate shadowing length is required to avoid that nanowires bundle together as they grow in height. Then, the orientation of the initial single-crystalline nuclei will be preserved as the nuclei develop to singlecrystalline nanowires.

2.2. Texture Analysis of Nanowire Ti Thin Films

The influence of the substrate temperature (77 K $\leq T_{Sub} \leq$ 873 K) on the distribution of the crystal orientations in the obliquely deposited Ti thin films ($\theta_{OAD} = 82^{\circ}$) is investigated by X-ray in-plane pole figure (IPPF) measurements. The film thickness calibrated for vertical particle incidence ($\theta_{OAD} = 0^{\circ}$) is 4 µm, meaning that for all samples, the same amount of material is evaporated. The actual film thickness is determined from the cross-sectional SEM images, as shown in Figure 1. For the IPPF measurements, the Bragg reflections corresponding to the Ti{0002} (*c*-planes) and Ti{10-10} (*m*-planes) are used. During measurement, the samples are aligned in the X-ray diffraction goniometer so that $\Phi = 270^{\circ}$ corresponds to the incident flux direction, as indicated by the black arrows in **Figure 8**g,h.



Figure 8. Measured X-ray IPPFs for the hcp Ti{0002} and Ti{10-10} reflections of obliquely deposited Ti thin films at $\theta_{OAD} = 82^{\circ}$ and with varying substrate temperatures: a,b) $T_{Sub} = 77$ K, c,d) $T_{Sub} = 485$ K, e,f) $T_{Sub} = 679$ K, and g,h) $T_{Sub} = 873$ K. The intensity is depicted on a linear scale and applies for all measured pole figures. The black arrows in (g) and (h) indicate the direction of the incoming particle flux.



The diffracted intensity of the measured pole figures is scaled linear and applies for all measured pole figures (Figure 8a-h).

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For deposition at 77 K, the corresponding pole figure in Figure 8a unveils a distinct pole density maximum at $(\Phi = 270^\circ, \chi = 37^\circ)$ as well as a density ring at $(\Phi = [65^\circ, 0^\circ],$ $\chi = 83^{\circ}$). Consequently, two components of crystals (texture components^[19]) are present. The hcp crystals that exhibit a *c*-axis pointing toward the direction of the incoming particle flux characterize the first texture component. Precisely, the crystals' c-axis is tilted by an angle of $\gamma_{[0001]}=37^\circ$ with respect to the substrate normal. These crystals are confined in polar direction, but there is no additional restriction in azimuthal direction, as suggested by the density ring in the pole figure in Figure 8b, meaning that the first component of crystals exhibits a fiber texture. For the second texture component, a fiber texture is given as well, because the crystals' *c*-axis is confined on a fixed polar angle, $\gamma = 83^{\circ}$, around another virtual center. Summarizing, two fiber textures are observed in the nanowire Ti thin films deposited at 77 K.

With increasing substrate temperature, more well-separated pole density maxima are detected. As shown in Figure 8c, three pole density maxima are obtained for deposition at 485 K: ($\Phi = 270^{\circ}$, $\chi = 45^{\circ}$), ($\Phi = 270^{\circ}$, $\chi = 88^{\circ}$), and ($\Phi = 90^{\circ}$, $\chi = 88^{\circ}$). For the crystals represented by the first pole density maximum, the *c*-axis is inclined by $\gamma_{[0001]} = 45^{\circ}$. In contrast, for the crystals represented by the latter two pole density maxima, the *c*-axis is aligned nearly horizontally with respect to the substrate surface. Additionally, Figure 8d shows clearly distinguishable pole density maxima connected by a weaker density ring, thus confirming an azimuthal confinement of the *m*-axis of the hcp crystals.

Figure 8e shows the obtained pole figure for deposition at 679 K, which includes three pole density maxima: ($\Phi = 270^{\circ}$, $\chi = 28^{\circ}$), ($\Phi = 270^{\circ}$, $\chi = 88^{\circ}$), and ($\Phi = 90^{\circ}$, $\chi = 88^{\circ}$). Comparing these with the pole density maxima obtained in Figure 8c leads to the following observations: 1) the tilt of the crystals' *c*-axis for the first crystal component changes with enlarged substrate temperature from $\gamma_{[0001]} = 45^{\circ}$ to $\gamma_{[0001]} = 28^{\circ}$ and 2) the *c*-axis of the second and third crystal component is aligned parallel to the substrate surface, and the crystals' *m*-axis becomes less confined in azimuthal direction as the substrate temperature

is increased. This azimuthal distribution is not random, because four separated pole density maxima are shown in Figure 8f at ($\Phi = 0^{\circ}$, 55°, 125°, 180°, $\chi = 88^{\circ}$). A low-density ring connects these pole density maxima. Hence, Ti thin films deposited obliquely at 485 and 679 K exhibit a biaxial texture with fiber contribution.

The IPPFs for deposition at 873 K are shown in Figure 8g,h. At ($\Phi = 270^{\circ}$, $\chi = 29^{\circ}$), a pole density maximum is detected that corresponds to the component of crystals whose *c*-axis is tilted by $\gamma_{[0001]} = 29^{\circ}$. Crystals with *c*-axis aligned nearly parallel to the substrate surface are represented by the remaining six pole density maxima at ($\Phi = 20^{\circ}$, 90° , 149° , 200° , 270° , 332° , $\chi = 88^{\circ}$). Especially, the pole density maxima in Figure 8h are remarkably extended in azimuthal direction, meaning that the confinement of the *m*-axis in that direction vanishes. Thus, a biaxial texture with strong fiber contribution is observed.

In summary, obliquely deposited Ti thin films grown at 485 K ($T_{\rm H} = 0.25$) and 679 K ($T_{\rm H} = 0.35$) exhibit a biaxial texture with minor fiber contributions. Fiber texture components become more pronounced for low substrate temperatures ($T_{\rm Sub} = 77$ K, $T_{\rm H} = 0.04$) as well as for high substrate temperatures ($T_{\rm Sub} = 873$ K, $T_{\rm H} = 0.45$).

The previously outlined investigations have shown that in total two texture components could be detected for the investigated substrate temperatures: 1) components with the *c*-axis tilted away by an angle $28^{\circ} \leq \gamma_{(0001)} \leq 45^{\circ}$ with respect to the substrate normal and 2) components with the *c*-axis aligned nearly parallel to the substrate surface. For component (1), the dependence of the γ_{100011} angle on the substrate temperature is analyzed in more detail. In addition, in a previous study,^[14] it was reported that the $\gamma_{[0001]}$ angle for nanowire Ti thin films grown at RT is also influenced by the angle of the incoming particle flux θ_{OAD} . **Figure 9**a shows the dependence of the $\gamma_{[0001]}$ angle on the angle of the incoming particle flux (76° $\leq \theta_{OAD} \leq 88^{\circ}$, $T_{Sub} = 300 \text{ K}$ fixed). For comparison, the corresponding nanowire tilt angles β measured with respect to the substrate normal are also included in this figure. The difference between both angles $\Delta = \beta - \gamma_{[0001]}$ as a function of the incoming flux direction is shown in Figure 9b.

From Figure 9a, it can be deduced that β is larger than $\gamma_{[0001]}$, and both angles are increased as the incidence flux direction



Figure 9. a) Tilt angle of the *c*-axis of the hcp crystallites $\gamma_{[0001]}$ and tilt angle β of the Ti nanowires obliquely deposited at RT for varying angles of the incoming particle flux θ_{OAD} . b) Difference Δ between β and $\gamma_{[0001]}$ depending on θ_{OAD} .



becomes more oblique. Moreover, from Figure 9b, it can be derived that Δ remains approximately constant at $\Delta \approx 9^{\circ}$ as the incidence angle is varied between $76^{\circ} \leq \theta_{OAD} \leq 88^{\circ}$. The observation that the lattice planes in the nanowires are not necessarily aligned with the tilt angle of the nanowires has already been reported by Moon and Shin^[20] for Co/Pt multilayer thin films. Contrary to that, the *c*-axis of the hcp crystallites in the Co–Cr magnetic thin films is aligned with the nanowire growth direction, as reported by Hagemeyer et al.,^[21] indicating a strong material-dependent component for the texture formation.

According to van der Drift,^[13] among initially randomly oriented crystals, those with the fastest vertical growth component will be successful in the competitive growth process. In the following paragraphs, an expression is derived that enables to roughly estimate for which tilt angle γ_{100011} of the *c*-axis of the hcp crystals the fastest vertical growth for a fixed incidence angle would be expected. The *c*-plane is the thermodynamically favored crystal plane (minimal surface energy) in a hcp crystal. Vertical particle incidence ($\theta_{OAD} = 0^\circ$) results in the growth of a crystalline layer with growth direction along a [0001] direction. As the substrate is tilted to oblique angles, the [0001] direction is inclined by an angle $\gamma_{[0001]}$ with respect to the substrate normal. This $\gamma_{[0001]}$ angle can be determined from the IPPFs and is known to be not equal to the angle of the incoming particle flux: $\gamma_{[0001]} \neq \theta_{OAD}$. As a result, the amount of material flux (particles per unit area) reaching the *c*-plane is reduced by the factor cos $(\theta_{\text{OAD}} - \gamma_{[0001]})$, premising that the adatom cannot reach other lattice planes (see Figure 10). An additional reduction by the factor cos (γ_{100011}) is given, because the crystal growth along [0001] also leads to a reduced growth along the substrate normal. Thus, if the product (cos ($\gamma_{[0001]}$) × cos ($\theta_{OAD} - \gamma_{[0001]}$)) becomes maximal, the crystal tilted by an angle $\gamma_{[0001]}$ is expected to have the maximal vertical growth component, indicating that $\gamma = \frac{1}{2} \times \theta_{OAD}$.^[13] This 2D approach is only based on geometrical considerations and does not consider other factors that influence the crystal growth, for instance, surface self-diffusion. Neverthe less, Figure 9a confirms that the measured $\gamma_{[0001]}$ angles are in good agreement with the predicted $\gamma_{[0001]}$ angles for maximized vertical growth: $\gamma = \frac{1}{2} \times \theta_{OAD}$ (compare dotted blue line). It has been confirmed that during film growth, the crystals that exhibit an angle $\gamma_{[0001]}$ that ensures a maximized vertical growth component are selected, which is in accordance with the evolutionary selection process introduced by van der Drift.^[13] Crystals with other $\gamma_{[0001]}$ angles will capture less material during growth and therefore will be overgrown, as shown in Figure 10.



Figure 10. Schematic illustration of tilted crystallites grown on an amorphous SiO₂ substrate at a highly oblique angle θ_{OAD} . The adatom mobility is restricted to a particular lattice plane. The crystallites are tilted by an angle γ . All angles are measured with respect to the substrate normal. The shadowed areas are shaded.



To understand why the tilt angle of the crystals *c*-direction differs from the nanowires' tilt angles ($\gamma_{100011} \neq \beta$), shadowing must be considered. Caused by the extreme shadowing conditions as present for highly oblique incidence angles, the atoms of the layers in the nanowire become shadowed as the growth process proceeds. For schematic illustration, see Figure 11a. As deposition is performed at highly oblique angles, a particle arriving at the growing layer (growth zone) causes the creation of a shadowed area (marked as the shaded area in the illustration). In particular, the particle in blue color impedes later arriving particles to condense in the shadowed area projected behind this particle. Consequently, the layer is shortened, compared with the underlying layer in the direction of the incoming particle flux, causing the formation of a step-like structure. Toward the incoming particle flux direction, the growth of the layer is completed by the particle in red; thereby, an overhang structure is formed. This overhang develops until the shadowed area created by the blue particle of the before-standing crystal is reached (compare (II) and (III)). Finally, a tilted nanowire composed of layers is formed, as shown in Figure 11b. Of course, assuming strong enough surface diffusion, a single particle cannot impede the condensation of another incoming particle in its shadow, as the new particle may simply diffuse around the already deposited particle. Nevertheless, the probability of becoming deposited in such a shadowed area is reduced with the same consequences. Notice that the effect will not be as regular as shown in Figure 11. Additionally, the shadowing of the layers in a nanowire is a process based on a large number of particles. Each of these processes is individually according to the particle divergence and the resulting shadowing effect, but on average, it is expected that the shadowing of the layers follows the principle as shown in Figure 11a. It can be noted that among randomly oriented crystallites, those that are selected are those that grow along the thermodynamically favored [0001] direction with a γ_{00011} tilt angle that ensures the maximized vertical growth. The β tilt angle of the nanowire is determined by shadowing.

Figure 12 shows a) the dependence of the $\gamma_{[0001]}$ angle on the substrate temperature (77 K \leq $T_{\rm Sub}$ \leq 873 K, $\theta_{\rm OAD}$ = 82° fixed) as well as b) the difference $\Delta = \beta - \gamma_{[0001]}$ as a function of the substrate temperature. The following observations can be made. First of all, the tilt angle β is again larger than the tilt angle of the crystals *c*-direction $\gamma_{[0001]}$. Second, the obtained $\gamma_{[0001]}$ angles scatter around the arithmetic mean value $\gamma_{[0001]} \approx 36^{\circ}$. This is near the predicted angle for a maximized vertical growth $\gamma = \frac{1}{2} \theta_{OAD} = 41^{\circ}$. In contrast, the β angles scatter around the arithmetic mean value $\beta \approx 60^{\circ}$. Third, $\Delta = \beta - \gamma_{[0001]}$ decreases from $\Delta = 26^{\circ}$ to $\Delta = 3^{\circ}$ between 77 K $\leq T_{Sub} \leq$ 485 K. Moreover, it can be noted that a temperature change from 77 to 485 K results in a larger change of the nanowire tilt angles $(48^{\circ} \le \beta \le 63^{\circ})$ than for the tilt of the crystal *c*-direction $(37^{\circ} \leq \gamma_{[0001]} \leq 45^{\circ})$. For a further temperature rise, larger β angles, but smaller γ angles, can be observed so that the difference between both angles increases up to $\Delta = 41^{\circ}$ for 873 K $(T_{\rm H} = 0.45).$

It has been demonstrated that the differences in crystallinity and texture of the Ti thin films deposited at varying substrate temperatures originate from the competition between the shadowing length determined by the highly oblique deposition angle (here $\theta_{OAD} = 82^{\circ}$) and the adatom mobility length, which is a

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Figure 11. a) Schematic to illustrate the shadowing of the layers in the nanowire and the resulting formation of the nanowires' tilt angle β for highly oblique incidence angles θ_{OAD} (green arrow, I–III). Shadowed areas are shaded. Behind the particle in blue color, the following particles cannot condense caused by shadowing. The red particle denotes the particle that completes a growing layer, thereby forming an overhang structure (for details, see text). b) Schematic to illustrate the geometric relations of the tilt angle β , tilt of the crystallites direction γ , and incidence angle θ_{OAD} for a tilted nanowire composed of layers. All angles are measured with respect to the substrate normal. The resulting shape of the nanowire is indicated by the dotted envelope.



Figure 12. a) Tilt angle of the *c*-axis of the hcp crystallites $\gamma_{(0001)}$ and tilt angle β of Ti columns obliquely deposited at an angle of the incoming particle flux $\theta_{OAD} = 82^{\circ}$ for varying substrate temperatures T_{Sub} . b) Difference Δ between β and $\gamma_{(0001)}$ depending on T_{Sub} .

thermally activated process that increases exponentially with substrate temperature. The TEM data presented in the first part have shown that polycrystalline nanowires are formed at 77 K. This leads to the conclusion that although the substrate temperature is low, there might be still adatom mobility present enabling the growth of those polycrystalline nanowires. However, the jump rate Γ is low in this temperature range, meaning that morphology evolution is mainly guided by the self-shadowing effect as the shadowing length dominates the self-diffusion length. Because shadowing is extreme and the adatom mobility is highly limited, a fiber texture is observed.

It is known that by increasing the substrate temperature, the jump rate Γ of the adatoms is enlarged

$$\Gamma(T_{\text{Sub}}, E_A) = \nu_o \exp\left(-\frac{E_A}{k_B T_{\text{Sub}}}\right)$$
(1)

The vibration frequency is denoted as v_0 , k_B is the Boltzmann constant, and the activation energy for surface self-diffusion is

 $E_{\rm A}$. As the vibration frequency v_0 is approximately constant ($\approx 10^{13}$ Hz), the relation between jump rate and vibration frequency Γ/v_0 is enlarged with increasing temperature T_{Sub} . Comparing the SEM images in Figure 1 for deposition at 485 and 679 K unveils a significant morphological change of the nanowires. As only the substrate temperature has been increased while all other deposition parameters have remained equally, a remarkable increase for the Γ/v_0 relation is expected for $T_{\rm Sub} > 485$ K. Consequently, the adatom mobility length will increasingly dominate the shadowing length. For deposition at 485 K, the adatom mobility is large enough that enables the growth of single-crystalline nanowires, but shadowing is expected to have still a strong impact on the growth process. Such a balance between both shadowing and adatom selfdiffusion length is assumed to facilitate the growth of a biaxially textured thin film composed of single-crystalline nanowires. Further increasing the substrate temperature is accordingly expected to significantly enlarge the Γ/ν_0 relation so that the crystals grow according to their crystal habit, leading to the growth of



single-crystalline structures as well, but the high-aspect-ratio nanowires that are typical for OAD cannot be obtained anymore. At this stage, shadowing no longer dominates the growth, and a fiber texture will be formed as observed for deposition at $T_{\rm Sub} = 873$ K ($T_{\rm H} = 0.45$).

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For a more quantitative discussion, information concerning the adatom mobility of Ti adatoms in the studied temperature range between 77 and 873 K is required. Up to now, diffusion coefficients for temperatures >1200 K were determined.^[16,17] As a matter of fact, the diffusion coefficients cannot simply be extrapolated to such low temperatures as used for the present study. Moreover, even at 77 K substrate temperature, it is not possible to completely disregard the influence of surface selfdiffusion, as the present work and our comparative study of different metals deposited at low and elevated substrate temperatures indicate.^[22] In the following paragraphs, an ansatz is presented that allows a quantitative estimation of the average adatom surface self-diffusion length.

Some authors^[23–25] maintain that there is a linear dependence between activation energy E_A for bulk self-diffusion and melting point of the metal. According to Mehrer,^[25] the activation energy of bulk self-diffusion for metals is given by

$$E_{A,\text{Bulk}} = m \cdot k_{\text{B}} \cdot T_{\text{Melt}} \tag{2}$$

with the slope m = 17.6 of the linear fit for the E_A-T_{Melt} relation (see **Figure 13**). Excepting that a linear dependence between the activation energies for bulk self-diffusion and the melting point exists, it can also be presumed that such a relation might exist for the average activation energies for surface self-diffusion (i.e., if the activation energies for all planes of a crystal are averaged). Figure 13 indeed shows a linear dependence of those average activation energies for surface self-diffusion on the melting point, expressed by $E_{A, Surface} = 9.5 k_B T_{Melt}$.

The self-diffusion length Λ of an adatom is given by the surface diffusivity D_S and the diffusion lifetime τ : $\Lambda = 2\sqrt{D_S \cdot \tau}$.



Figure 13. Average activation energies E_A of metals for bulk (black) according to Mehrer^[25] and surface self-diffusion (red) versus the material melting point T_{Melt} . The activation energies for the surface self-diffusion were taken from the literature: Al,^[26] Cu,^[27] Ni,^[28] Ti,^[29] Pt,^[30] Nb,^[30] Mo,^[31] Ta,^[31] and W.^[32]

Assuming that the mobility lifetime τ corresponds to the time interval Δt between the deposition of successive monolayers, this time interval depends on the growth rate $g_{\rm D}$, the atomic area density (atoms per unit area) *N*, and the atomic volume Ω

$$\Delta t = N \cdot \frac{\Omega}{g_{\rm D}} \tag{3}$$

It is known that the temperature-dependent diffusivity D_S can be expressed by

$$D_{\rm s} = D_0 \cdot \exp\left(\frac{-E_{\rm A}}{k_{\rm B}T_{\rm Sub}}\right) \tag{4}$$

 D_0 is a pre-exponential factor. Combining Equation (2), (3), and (4) yields the following expression for the adatom self-diffusion length Λ by

$$\Lambda = 2 \sqrt{\frac{D_0 \cdot N \cdot \Omega}{g_D \exp\left(\frac{-E_A}{k_B T_{\text{Sub}}}\right)}}$$
(5)

The adatom surface self-diffusion length Λ is estimated exemplarily for Ti. Assuming $D_0 = 3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1,[30]} N = 1.5 \times 10^{19} \text{ m}^{-2}$, $g_D = 1 \times 10^{-9} \text{ m}$, $\Omega = 1.2 \times 10^{-29} \text{ m}^3$, and $E_A = 1.3 \text{ eV}$,^[29] Equation (4) yields $\Lambda \approx 1 \times 10^{-37} \text{ nm}$ for $T_{\rm Sub} = 77 \text{ K}$ ($T_{\rm H} = 0.04$), $\Lambda \approx 5 \times 10^{-6} \text{ nm}$ for $T_{\rm Sub} = 300 \text{ K}$ $(T_{\rm H} = 0.15), \quad \Lambda \approx 0.08 \, {\rm nm} \quad {\rm for} \quad T_{\rm Sub} = 485 \, {\rm K} \quad (T_{\rm H} = 0.25),$ $\Lambda \approx 7 \text{ nm}$ for $T_{\text{Sub}} = 679 \text{ K}$ ($T_{\text{H}} = 0.35$), and $\Lambda \approx 82 \text{ nm}$ for $T_{\rm Sub} = 873$ K ($T_{\rm H} = 0.45$). Indeed, these calculated data for deposition at 77 K do not suggest an adatom mobility that allows the formation of polycrystalline nanowires. Moreover, these calculations do not allow to explain why for 77 K a fiber texture is observed but for 300 K a mainly biaxial texture. However, those values are supposed to be systematically underestimated, because the surface of the growing nanowires is expected to exhibit parts withca large surface curvature, e.g., which is not considered by Equation (5). Nevertheless, for deposition at higher substrate temperatures (from 485 to 679 K), an increase for the adatom self-diffusion length by a factor of 100 is predicted. This might account for the observed significant morphological changes for deposition at 485 and 679 K. In addition, it should be pointed out that with increasing T_{Sub} , the homologous temperature approaches $T_{\rm H} \approx 1$, which is correlated with an increasing influence of bulk self-diffusion that has to be considered as well.

3. Conclusions

Ti thin films are grown under highly oblique deposition angles with substrate temperatures varying between 77 and 873 K. The structure of individual Ti nanowires and columns is analyzed by TEM measurements. For deposition at 77 K, the structure of the Ti nanowires is polycrystalline. For deposition at 300 K and for elevated temperatures, the formation of large crystals is observed, indicating a single-crystalline growth. The formation of branched nanowires could be attributed to an increased working pressure during deposition, indicating that the formation of unbranched, single-crystalline nanowires on amorphous substrates at RT

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requires low working pressures. Additionally, an adequate surface self-diffusion length and shadowing length have been identified as crucial parameters for the formation of single-crystalline nanowires.

X-ray IPPF measurements have been carried out to examine the texture of the thin films depending on the substrate temperature. A biaxial texture could be detected for highly oblique deposition at 300 and 485 K, but for $T_{\rm Sub}$ = 77 K and $T_{\rm Sub}$ ≥ 679 K, a fiber texture is observed. Hence, the formation of a biaxial textured thin film requires extreme shadowing conditions^[14] in combination with an adequate surface self-diffusion length. Moreover, two crystal components are present in the obliquely deposited Ti thin films. One component represents the hcp crystals with the *c*-axis oriented nearly parallel to the substrate surface, whereas for the other component, the *c*-axis is inclined toward the direction of the incoming flux direction. For the latter component, the tilt angle β has been found to be always larger than the tilt of the *c*-axis $\gamma_{[0001]}$. Reasons for this are the evolutionary selection processes of the fastest growing crystals (defining γ) in combination with the extreme shadowing conditions as present for highly oblique deposition angles (defining β). Furthermore, the incidence angle and the substrate temperature influence the tilt angle of the crystals' c-axis. To estimate the average surface self-diffusion length quantitatively, a linear dependence between average activation energy for surface selfdiffusion and melting point of the metals has been presumed.

4. Experimental Section

Sample Fabrication: Ti pellets (purity 99.995%) were evaporated by an electron beam. The base pressure in the vacuum chamber was $\approx 10^{-6}$ Pa, and the work pressure was in the range of $\approx 1 \times 10^{-6}$ Pa. The incidence angle θ_{OAD} was varied between 76° and 88° (measured with respect to the substrate normal). The deposition rate was kept constant at 1 nm $\rm s^{-1}$ at the substrate. Film thickness and deposition rate were both controlled by a quartz crystal microbalance. A continuous flow of liquid nitrogen (LN₂) through a Cu-block sample holder enabled reducing the substrate temperature down to 77 K. Two independent K-type thermocouples were mounted directly on the surface of the LN₂ sample holder for substrate temperature control. Additionally, a further K-type thermocouple was directly put into LN₂ to ensure a precise calibration. During deposition with the LN₂ sample holder, the substrate temperature was kept constant at 77 \pm 1 K. Increasing the substrate temperature from RT up to 873 K was performed using another sample holder that contained a computercontrolled tungsten wire resistance heater. The distance between crucible and sample holder was 35 cm for the LN₂-cooled sample holder and 30 cm for the holder with the heating system. As substrates, thermally oxidized, planar Si pieces (800 nm-thick oxide layer) were used. The Si pieces with sizes of $\approx 1 \times 1$ cm² were attached on the substrate holders with carbon glue. The carbon glue was left to dry overnight.

Sample Characterization: All samples were analyzed by SEM at an operating voltage of 3 kV to analyze the morphology. Cleaving the samples before SEM measurements enabled to obtain cross-sectional images of the samples. The nanowires' tilt angles as well as the film height with respect to the substrate normal were determined manually directly from these cross-sectional SEM images. A considerably large number of measurements were conducted to ensure a statistical reliability of the results.

The texture of the Ti thin films was analyzed ex situ by X-ray diffraction IPPF measurements using the in-plane degree of freedom of the detector arm and collimated Cu K α radiation with wavelength $\lambda = 0.15418$ nm (parallel beam geometry). For the pole figure measurements, the Ti(10-10) Bragg reflection ($2\theta = 35.093^{\circ}$) and the Ti(0001) reflection

 $(2\theta=38.421^\circ)$ were chosen.^[33] To scan the half sphere above the sample with fixed Bragg reflection geometry, the sample rotated around its normal by the azimuthal angle Φ [0°, 360°], and additionally, the diffraction plane was tilted with respect to the sample normal by the polar angle χ [0°, 90°]. The step sizes of both motions were 2°. As a result of this measurement, a diffracted intensity distribution as a function of Φ and χ was detected. This was plotted in stereographic projection to obtain the pole figure of the chosen Bragg reflection. All pole figures in the present study are as measured.

For TEM analysis, a Titan³ G2 60–300 microscope operating at 300 kV acceleration voltage was used. The cross-sectional specimen was fabricated using a focused high-energy Ga-ion beam and subsequent milling with low-energy Ar ions.^[16] NBED, selected area electron diffraction, as well as HRTEM were applied to study the crystallinity of individual Ti nanowires and columns in the cross-sectional specimen. Furthermore, specimens of single Ti columns were collected on lacey carbon-covered Cu grids by scratching the grid over the sample. No solvents were applied. The TEM images shown here are contrast enhanced.

Acknowledgements

S.L.-G. would like to thank the graduate school BuildMoNa and C.G. gratefully acknowledges the DFG project RA 641/23-1.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

biaxial textures, nanostructured surfaces, oblique angle deposition, single crystallines, tilt angles, titanium nanowires

Received: July 29, 2019 Revised: November 4, 2019 Published online: December 12, 2019

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