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The shape of epitaxially grown silicon nanowires and the influence of line tension

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ABSTRACT Silicon nanowires grown epitaxially via the vapor–liquid–solid mechanism show a larger diameter at the base of the nanowire, which cannot be explained by an overgrowth of the nanowire alone. By considering the equilibrium condition for the contact angle of the droplet, the Neumann quadrilateral relation, a quasi-static model of epitaxial nanowire growth is derived. It is found that a change of the contact angle of the droplet is responsible for the larger diameter of the nanowire base, so that the expansion has to be considered a fundamental aspect of epitaxial vapor–liquid–solid growth. By comparison of experimental results with theoretical calculations, an estimate for the line tension is obtained. In addition, the growth model predicts the existence of two different growth modes. Only within a certain range of line-tension values is the mode corresponding to ordinary nanowire growth realized, whereas nanowire growth stops at a relatively small height if the line tension exceeds an upper boundary. An approximate analytic expression for the upper boundary as a function of the surface tensions is given.

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1 Introduction

The prospect that nanowires could serve as components for future electronic or opto-electronic devices has recently drawn an extensive attention to the field of nanowires in general and silicon nanowires in particular [1]. The most promising candidates are epitaxially grown silicon nanowires, since the problem of integrating the nanowires into a certain device architecture could in principle be solved most elegantly by growing each nanowire directly at its final position on a silicon wafer. Of course there are additional requirements to be fulfilled. Probably the most important ones are a controlled doping of the silicon nanowires in combination with a precisely defined nanowire height and diameter. Unfortunately, experience shows that these three parameters are not independent of each other, so that a deeper understanding of the interdependences is necessary in order to grow silicon nanowires epitaxially and to meet all the requirements. This paper is a step in this direction.

In the first part we want to concentrate on the shape, that is the diameter as a function of the height, of silicon nanowires grown epitaxially via the vapor–liquid–solid (VLS) growth mechanism. Interestingly, the diameter is not constant over the entire length, but larger at the base of the nanowire, where it is grown onto the substrate. From a technological point of view, this larger diameter is an important detail of epitaxial nanowire growth. We will show that this larger diameter of the nanowire base is a consequence of epitaxial growth via the VLS mechanism, and that it results from the balance of forces acting on the droplet. Considering the equilibrium condition for the contact angle of the droplet, we will derive a quasi-static model of epitaxial nanowire growth. A comparison of the experimentally observed and the theoretically predicted nanowire shapes will allow us to get an estimate for the value of the line tension of the three-phase line.

The influence of the line tension on the shape of the nanowire will be the subject of the second part. This is an important aspect for the doping of the nanowire. The most common dopants are known to be very surface-active substances, so they will have a strong influence on the surface tensions and on the line tension, and consequently also on the shape of the nanowire. In the framework of a quasi-static growth model, an upper boundary τ'_{up} for the normalized line tension is found, beyond which regular nanowires cannot grow. This upper boundary might impose a technologically important restriction for the doping of silicon nanowires.

2 Quasi-static growth model

It has often been stated that the diameter of the nanowires grown via the VLS mechanism is determined by the size of the droplet. This is undoubtedly true, but it does not necessarily imply that the diameter of the nanowire is constant. In fact, the diameter of epitaxially grown silicon nanowires varies, especially in the region close to the substrate where the nanowires exhibit a larger diameter. One first guess would be that this larger diameter is created by an overgrowth of the nanowire after axial growth. However, an overgrowth

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alone does not provide a sufficient explanation for the observed phenomenon, for two reasons. The first reason, also put forward by Givargizov [2], is that the phenomenon of a larger diameter of the nanowire base occurs independent of the growth temperature. An overgrowth requires the supply of silicon, either by the vapor–solid mechanism and/or by surface diffusion. Both mechanisms are strongly temperature dependent so that the larger diameter of the nanowire base should change considerably at lower temperatures, which is not the case. The second reason is that the diameter enlargement of the nanowire base approximately scales with the diameter of the nanowire. If the diameter increase close to the base were only due to an overgrowth of the nanowire, one would expect its magnitude to be more or less diameter independent. Since these arguments show that the larger base diameter cannot be explained alone by an overgrowth after nanowire growth, it must be a result of nanowire growth itself. We will see that this is indeed the case. Nevertheless, especially at elevated temperatures, surface diffusion and vapor–solid growth might influence the shape of the diameter enlargement of the nanowire base. In particular, a faceting of the nanowire base expansion, often observed at high temperatures, might occur after growth by surface diffusion.

Before presenting a model to describe the growth of epitaxial nanowires in detail, we first take a look at the initial conditions of silicon nanowire growth. We assume that the silicon nanowires are growing epitaxially on a flat silicon surface, that gold is used as the catalyst material, and that growth takes place via the VLS mechanism. So growth starts with a Au/Si-eutectic droplet, sessile on the silicon surface, and the initial conditions for growth are determined by the properties of this Au/Si-eutectic droplet. Such a droplet is schematically depicted in Fig. 1a, where σ_l, σ_ls, and σ_s are the surface tension of the droplet surface, the liquid–solid interface tension, and the silicon surface tension, respectively. The droplet has a contact area of radius r_0 and a contact angle β_0, so that the radius R of the droplet can be expressed as $R = r_0/\sin(\beta_0)$. The contact angle β_0 can be related to the surface tensions and the line tension τ by

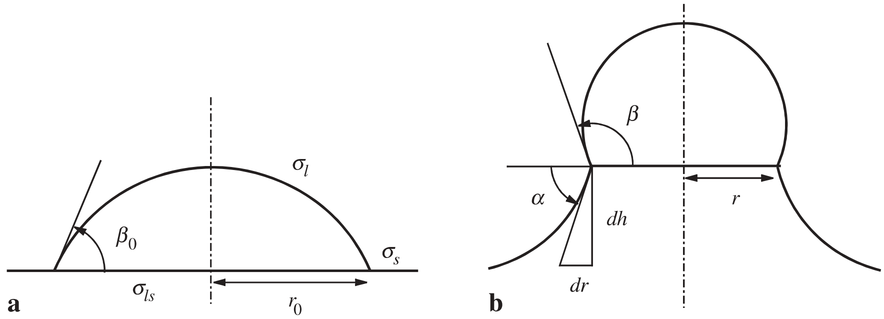

FIGURE 1 **a** Schematic of a Au/Si-eutectic droplet sessile on a flat surface. **b** Schematic of the initial stage of nanowire growth

a modified Young's equation [3]

$$\sigma_\mathrm{l}\cos(\beta_0) = \sigma_\mathrm{s} - \sigma_\mathrm{ls} - \frac{\tau}{r_0}\,. \tag{1}$$

We use the term 'modified', because a line-tension contribution has been added to Young's equation, as suggested by Pethica [4] and Widom [5]. Dealing with macroscopic droplets, the effect of the line tension can be neglected, but in our case, with radii in the nanometer range, the line tension cannot be omitted a priori. Equation (1) is the equilibrium condition for the contact angle β_0 and it reflects the balance of the forces acting on the droplet.

The solubility of gold in silicon as well as the evaporation rate of gold at typical growth temperatures are small, so that the volume of the Au/Si-eutectic droplet can be assumed to be constant during growth. Suppose that the shape of the droplet is given by a segment of a sphere; then the volume V of the Au/Si-eutectic droplet can be expressed as

$$V = \frac{\pi}{3}\left(\frac{r_0}{\sin(\beta_0)}\right)^3 (1-\cos(\beta_0))^2 \times (2+\cos(\beta_0))\,. \tag{2}$$

After the flow of the precursor gas is switched on, growth starts. The initial stage of growth is schematically depicted in Fig. 1b, where $h(\alpha)$ and $r(\alpha)$ are the height and the radius of the nanowire as a function of the inclination angle α of the nanowire flanks. By use of the Neumann quadrilateral relation [6], the contact angle β can be related to the surface tensions, the line tension τ, and the inclination angle α:

$$\sigma_\mathrm{l}\cos(\beta) = \sigma_\mathrm{s}\cos(\alpha) - \sigma_\mathrm{ls} - \frac{\tau}{r}\,. \tag{3}$$

One can see that in the limit $\alpha \to 0$, (3) becomes equal to (1), the modified Young's equation. In our case, where the nanowires are grown on a flat substrate, α equals zero at the beginning. As growth starts, the angle α has to increase. By considering (3) it becomes immediately clear that an increase of α is accompanied by an increase of β, which means that the droplet approaches a larger solid angle of a spherical section. But this causes a decrease of the contact area and a decrease of the radius r. Consequently, the final radius of the nanowire should be smaller than the initial radius r_0 of the contact area of the droplet or, in other words, the nanowire diameter is largest at the nanowire base.

In order to describe this development of the droplet, the fact that the droplet shape is assumed to be a segment of a sphere can be used to express the radius of the contact area r as a function of the contact angle β and the volume V:

$$r(\beta) = \left(\frac{3\,V}{\pi}\right)^{1/3} \times \frac{(1+\cos(\beta))^{1/2}}{(1-\cos(\beta))^{1/6}\,(2+\cos(\beta))^{1/3}}\,. \tag{4}$$

Additionally, we can make use of the fact that the inclination angle α of the nanowire flank, as indicated in Fig. 1a, can also be expressed as

$$\tan(\alpha) = -\frac{\mathrm{d}h(r)}{\mathrm{d}r}\,. \tag{5}$$

The minus sign in (5) arises since a decrease of the radius leads to an increase of $\tan(\alpha)$. This differential equation can directly be solved by integration, leading to an expression for $h(\alpha')$:

$$h(\alpha') = -\int_0^{\alpha'} \tan(\alpha)\left(\frac{\mathrm{d}r}{\mathrm{d}\alpha}\right)\mathrm{d}\alpha\,. \tag{6}$$

The derivative in the integrand above is easily found by using (3) and (4). Of course, the above expression for $h(\alpha)$, which is the central expression of our model, implicitly assumes that the physical process of growth proceeds as long as the equilibrium conditions for the droplet allow it. This means that the supply of silicon for the growth of the silicon nanowire is ensured, but that the speed of growth, on the other hand, is not too high so that the liquid droplet can always maintain its equilibrium shape. Another condition is that the supersaturation in the Au/Si-eutectic droplet is sufficiently high to overcome the Gibbs–Thomson effect due to the small radius of the droplet and the nanowire. We believe that the effect of supersaturation on the balance of forces can be neglected to a good approximation. The most significant consequence of supersaturation would be a slight change of the composition of the Au/Si-eutectic droplet, which then causes a small change of σ_l, the surface tension of the droplet. In a way, our growth model is a quasi-static model, since we are not referring to any time-dependent quantities. It is as much an analysis of the droplet shape as a model for nanowire growth. The advantage of this approach is that the number of unknowns is reduced to a minimum.

The only unknowns necessary to model the shape of the silicon nanowire are the values of the surface tensions and the line tension. Suppose that σ_l, the surface tension of the droplet, is approximately given as $0.85\,\mathrm{J\,m^{-2}}$ [7], and the specific surface energy of the $\langle 111 \rangle$ silicon surface $\sigma_s \approx 1.24\,\mathrm{J\,m^{-2}}$ [8]; then knowledge of the contact angle $\beta_0 \approx 43°$ [9] of a macroscopic droplet (the line tension is effectively zero) leads to a liquid–solid interface tension $\sigma_{ls} \approx 0.62\,\mathrm{J\,m^{-2}}$. Both the surface tensions and the line tension are taken to be isotropic; yet, an extension of the model to allow for anisotropy effects seems to be possible. Unfortunately, reliable data on the value of the line tension τ are not available, so that τ is left as a free parameter.

3 Results and discussion

To keep the following considerations as concise as possible, a set of dimensionless variables will be introduced here: two dimensionless surface tensions, $\sigma'_s \equiv \sigma_s/\sigma_l$ and $\sigma'_{ls} \equiv \sigma_{ls}/\sigma_l$, and a dimensionless line tension $\tau' \equiv \tau/r_0\sigma_l$. Note that the dimensionless line tension scales inversely with the contact radius of the droplet, leading to a vanishing line-tension contribution for macroscopic droplets.

The aforementioned surface-tension values give $\sigma'_s = 1.46$ and $\sigma'_{ls} = 0.73$. Using these values, and (3) and (4), a numerical evaluation of the integral in (6) then gives the height h as a function of the radius r. This function, i.e. the shape of half of a silicon nanowire, is depicted for some values of τ' in Fig. 2, where both the height and the radius are expressed in units of r_0. One can see in Fig. 2 that there are two different growth modes present. The first growth mode, shown in Fig. 2 for $\tau' = 0.08$ and $\tau' = 0.12$, results in hillock-like structures of finite height (see also Fig. 3b), whereas line-tension values being moderately positive, zero, or negative, lead to the expected and well-known nanowire growth (see also Fig. 3a). In this nanowire-growth mode, the radius of the nanowire shrinks within a finite height from r_0, the initial radius, to a radius close to the final radius $r_{fin} \approx 0.4\,r_0$ of the nanowire. Note that the curves for $\tau' = 0.04$, $\tau' = 0$, and $\tau' = -0.08$ would, for infinitely small numerical step size, extend to infinite height, which is schematically

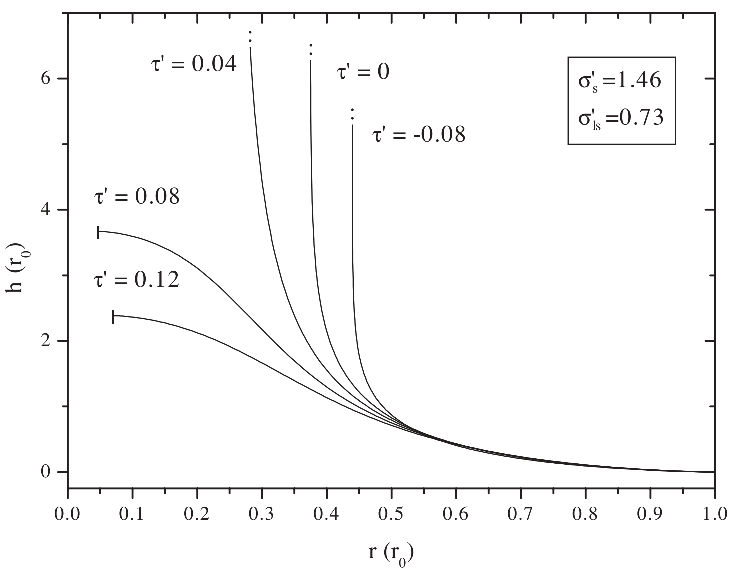

FIGURE 2 Silicon nanowire shape for various line-tension values τ'

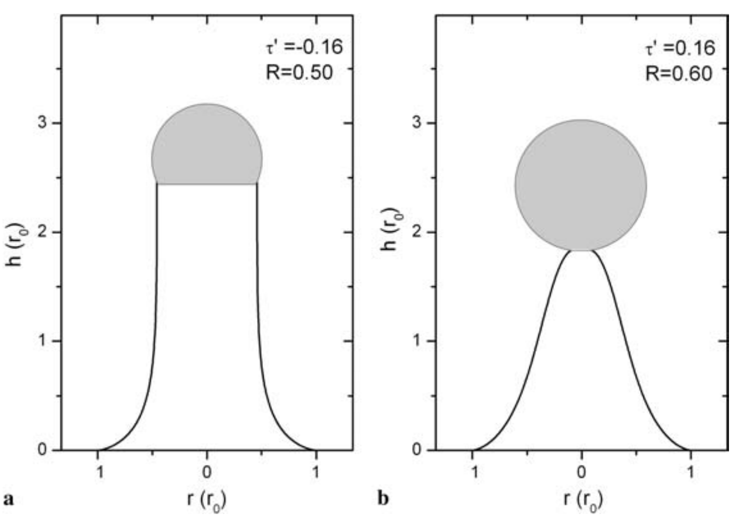

FIGURE 3 Calculated nanowire shapes for $\sigma'_{ls} = 0.73$ and $\sigma'_s = 1.46$: **a** normal nanowire growth, $\tau' = -0.16$ **b** hillock growth, $\tau' = +0.16$. The *gray shaded areas* represent the Au/Si-eutectic droplets having radius R

denoted by the two dots at the upper end of the curves. The transition from the initial stage to a growth with an almost constant radius $r \approx r_{\text{fin}}$ becomes sharper for smaller line-tension values. As an example, a comparison of the nanowire shapes corresponding to the two nanowire growth modes is schematically depicted in Fig. 3 for $\tau' = \pm 0.16$. The black curves in Fig. 3 correspond to the calculated silicon surface of the nanowire and the gray shaded areas represent the Au/Si-eutectic droplets of radius R.

In order to compare the calculated shapes of the nanowire close to its base to experimental results, a high resolution transmission electron micrograph (JEM-4010, viewing direction Si $[1\bar{1}0]$) of the base of a silicon nanowire is shown in Fig. 4. The nanowire in Fig. 4 has been produced by chemical vapor deposition in UHV environment via the VLS growth mechanism using gold as catalyst and diluted silane (5% in argon) as precursor gas. The gold was deposited in situ as a film of 0.2-nm thickness on a hydrogen-terminated, $\langle 111 \rangle$-oriented silicon wafer and subsequently annealed at 300 °C for 30 min. Nanowire growth takes place at a temperature around 400 °C at a silane partial pressure around 10 Pa. The transmission electron micrograph of Fig. 4 also clearly shows the epitaxial relation between the $\langle 111 \rangle$-oriented substrate and the nanowire. The white curve on the right flank of the nanowire is the calculated shape of the nanowire base for $\sigma'_s = 1.46$, $\sigma'_{ls} = 0.73$, and $\tau' = -0.12$. One can see that the calculation is in perfect agreement with the experimentally observed shape. Taking r_0 to be around 10 nm, the value of $\tau' = -0.12$ leads to an estimate for the line tension $\tau \approx -1 \times 10^{-9}\,\text{J}\,\text{m}^{-1}$. Using this value and recalling that the surface tensions are of the order $1\,\text{J}\,\text{m}^{-2}$, we can assign a width $\Delta l = |\tau|/\sigma \approx 1$ nm to the three-phase line, which seems to be of the right order of magnitude. Also, the negative sign of the line tension is not in contradiction to theory. Nevertheless, it must be emphasized that this is only a crude estimate for the line tension and that the errors of this estimate might be even larger than the estimate for τ' itself.

Coming back to the model, we have seen in Figs. 2 and 3 that there are two growth modes present. One corresponds to real nanowire growth (Fig. 3a) and the other leads to the growth of hillock-like structures (Fig. 3b). The transition from the nanowire to the hillock growth mode takes place if the line tension exceeds a certain upper limit τ'_{up}. This can be understood intuitively by considering that a positive line tension means that the energy of the system can be reduced by a shrinkage of the liquid–solid interface area. If the value of the line tension is too large, the impetus for a shrinking of the interface area becomes so strong that regular nanowire growth with constant radius becomes impossible. Instead, a further shrinkage of the contact area is preferred, which then leads only to the growth of the hillock-like structures shown for example in Fig. 3b. Note that the inclination angle α goes to zero as the height approached its final value, whereas the diminishing of the radius stops at a small but non-zero value. This is denoted in Fig. 2 by the vertical bar at the end of the curve. That the radius does not go to zero is reasonable, since a small contact area, to which the Au/Si-eutectic droplet is attached, has to be left. It should be mentioned here that a system with a droplet that is connected by such a small contact area is mechanically not very stable, and that it is not unlikely that the droplet may become disconnected from its base by minor mechanical forces.

The mathematical reason that one or the other growth mode is realized lies in the divergence of the integral in (6), or better in the divergence of $\tan(\alpha)$ in the integrand, as $\alpha \to \pi/2$. This is equivalent to the condition that $\cos(\alpha) = 0$ for $r = r_{\text{fin}}$, where $\cos(\alpha)$ is constrained by (3). If the line tension is positive and exceeds a certain limit τ'_{up}, the divergence of the integral disappears. The condition $\cos(\alpha) = 0$ cannot be fulfilled any more, the integral remains finite, and growth stops at a finite height. The interesting question is now at which line-tension value τ'_{up} does this transition take place? A short calculation gives the approximate solution

$$\tau'_{up} \approx \frac{2(1-\sigma'_{ls})^{3/2}}{3^{3/2}(1+\sigma'_s-\sigma'_{ls})^{1/2}}\,. \tag{7}$$

Taking the silicon values $\sigma'_s = 1.46$ and $\sigma'_{ls} = 0.73$ gives $\tau'_{up} \approx 0.04$, which is in agreement with the results shown in Fig. 2. In the case of a nanowire of $r_0 = 10$ nm this corresponds to a line tension $\tau \approx 3 \times 10^{-10}\,\text{J}\,\text{m}^{-1}$. This is a relatively small value, and it seems possible that in reality such a small line-tension value can be exceeded, with the consequence that normal nanowire growth is suppressed.

Although we explicitly referred to the growth of silicon nanowires with gold as catalyst, the validity of the model is in principle not restricted to this case. Especially, the addition of dopants to the Au/Si-eutectic droplet, for the growth of doped silicon nanowires, is of high technological importance. Since the dopants are known for being very surface active, i.e. for changing the values of surface tensions, an

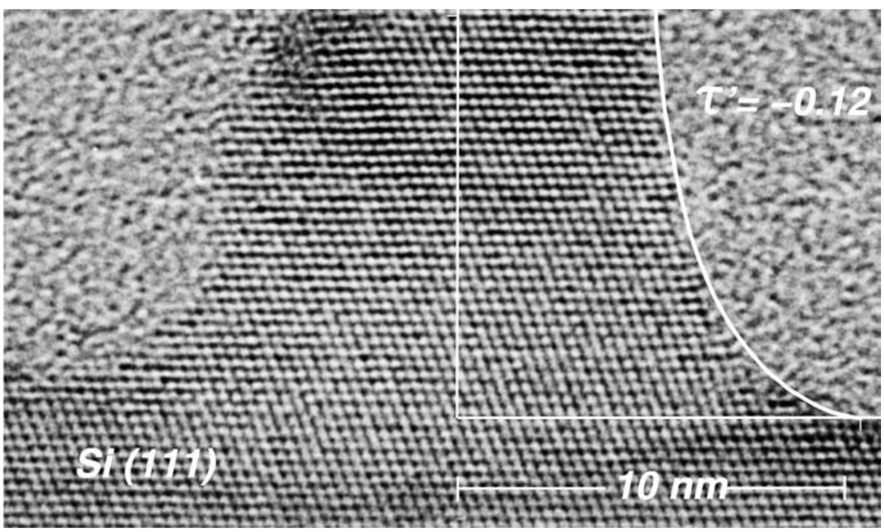

FIGURE 4 High resolution transmission electron micrograph of an epitaxially grown silicon nanowire. *White line*: calculated shape for $\tau' = -0.12$, $\sigma'_{ls} = 0.73$, and $\sigma'_s = 1.46$

analysis of the consequences of a variation of the dimensionless surface tensions σ'_s and σ'_{ls} is of interest. Although our model predicts two different growth modes, we want to concentrate on the nanowire-growth mode in the further discussion. In order to characterize the nanowire we choose the final nanowire radius r_{fin}, i.e. the radius at infinite height, as a characteristic parameter.

In Fig. 5 this parameter r_{fin} in units of r_0 is plotted as a function of the line tension τ' for various values of σ'_s, where the dimensionless interface tension $\sigma_{ls} = 0.73$ is kept constant at the value of the gold–silicon system. One can see that for all curves both an upper and a lower line-tension boundary exists, in between which nanowires with a final nanowire radius r_{fin} can grow. The value of r_{fin} is zero at the lower boundary and increases with increasing line tension until it reaches a maximum value. A further increase of the line tension leads to a decrease of r_{fin}, which ends at the upper line-tension boundary τ'_{up}.

The lower boundary τ'_{lo} is located at the negative line tension $\tau'_{lo} = \sigma'_s - \sigma'_{ls} - 1$. A negative line tension means that the energy of the system can be lowered by an increase of the liquid–solid interface area. Consequently, the initial radius r_0 of the Au/Si-eutectic droplet becomes larger as the line tension becomes more negative. For line-tension values below $\tau'_{lo} = \sigma'_s - \sigma'_{ls} - 1$, the initial droplet would spread over the whole substrate, meaning that $r_0 \to \infty$. It is clear that under these circumstances, r_{fin} measured in units of r_0, has to become zero. The upper boundary is given by τ'_{up}. This is the more interesting boundary, because the magnitude of τ' is smaller and this increases the probability that this boundary might be reached in real systems. Interestingly, the final nanowire radius r_{fin} does not become zero at the upper boundary. It can be shown that, to a good approximation, all of the r_{fin} values at the upper boundary lie on a straight line going through $\tau' = 0$ and having the slope $(3/2)(1-\sigma'_{ls})^{-1}$. This straight line is depicted in Fig. 5 as a dashed line.

The addition of surface-active impurities does not only change σ'_s, but also the value of the liquid–solid interface tension might be changed, for which the effect of a variation of σ'_{ls}, the dimensionless liquid–solid interface tension, has to be considered. In Fig. 6, the final nanowire radius r_{fin} is plotted for various values of σ'_{ls}, where the surface tension σ'_s is kept constant. One can see that the final radius r_{fin} of the nanowire is increasing for increasing σ'_{ls}, but the general behavior remains the same. For all values a lower and an upper line-tension boundary exist. Similar to the situation shown in Fig. 5, the values of r_{fin} at the upper boundary are approximately located on a smooth curve. This curve, depicted in Fig. 6 as a dashed line, can be expressed as $(3/2)((4\tau')^{1/3} - \tau')(2 + \sigma'_s - \tau')^{-1}$. So, we have to conclude that neither a variation of σ'_s nor of σ'_{ls} substantially affects the general behavior. The observation that an upper boundary, close to $\tau' = 0$, exists, remains valid. Even if the surface tensions change within a wide range, nanowire growth is suppressed if the line tension exceeds the value of the upper boundary τ_{up}. In fact, this might explain our observation that silicon nanowires, although growing without problems on lowly doped silicon wafers, typically cannot grow on highly doped silicon wafers (both p- and n-type, resistivity of the order $10^{-3}\,\Omega\,\text{cm}$). In addition to changes of the surface tensions, the higher concentration of the

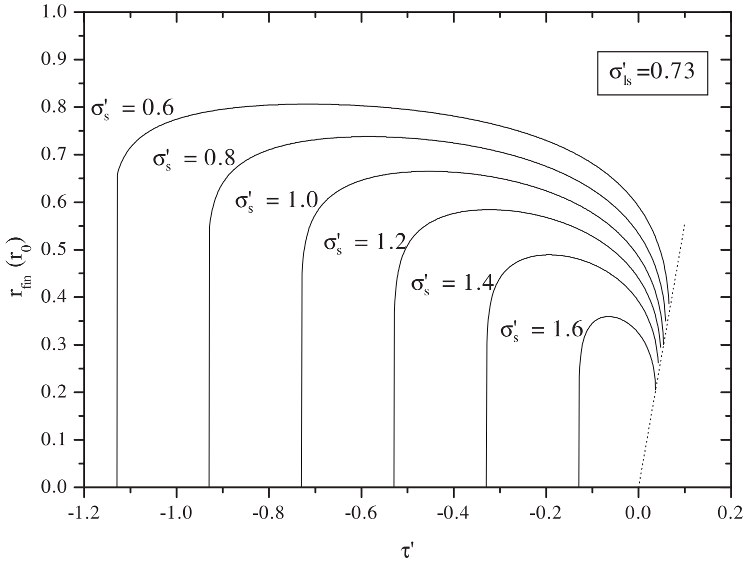

FIGURE 5 Final nanowire radius r_{fin} as a function of the line tension τ' for $\sigma'_{ls} = 0.73$ and various σ'_s values

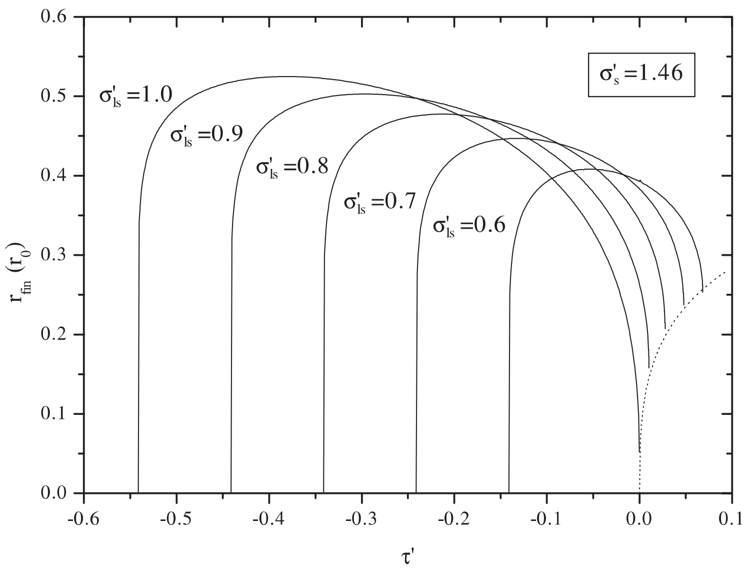

FIGURE 6 Final nanowire radius r_{fin} as a function of the line tension τ' for $\sigma'_s = 1.46$ and various σ'_{ls} values

dopant atoms, boron and arsenic, might have led to an increase in τ'. This increase of τ' over τ_{up} possibly induces a transition from one growth mode to the other, meaning an inhibition of nanowire growth.

4 Conclusion

In conclusion, we have shown that by considering the equilibrium condition for the contact angle of the droplet, the Neumann quadrilateral relation, a quasi-static growth model can be derived. The model explains the origin of the larger diameter of the base of the nanowire, which has been observed experimentally. By comparing the calculated shape of this expansion to a transmission electron micrograph, an estimate for the line tension was obtained. Furthermore, the model predicts that nanowire growth can only take place within a certain range of line-tension values. Analytic expressions for the upper and lower boundaries limiting this line-tension range have been given. The effect of changes of the surface tensions on the nanowire growth has been discussed. The model could possibly also explain our observation that silicon nanowires cannot grow on highly doped silicon wafers.

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