Is Ultra-Hardness Possible - a Brief Feasibility Study

Extended Edition

N. Schwarzer

Saxonian Institute of Surface Mechanics SIO, Tankow 2, 18569 Ummanz / Rügen,

Germany, www.siomec.de, n.schwarzer@siomec.de

Content

Abstract

A theoretical feasibility study will tackle the question whether or whether not it is possible to obtain hardness values higher than 100 GPa (so called "ultra hardness") for nano-composite TiN/a-Si_3N_4 and nano-composite TiN/a-Si_3N_4/$TiSi_2$ coating materials. For this an effective indenter concept is used which also takes into account the pressure induced increase of the Young's modulus and yield strength during indentation.

Also the question will be answered how hard those ominous and supposedly “ultra-hard” coatings being reported about rather a lot within the last decade really were if being considered and analyzed by the first principle methods elaborated here.

Last but not least, we are concentrating on giving explicit limits for lattice constant and effective interaction potentials necessary to reach hardnesses close or even higher than the one of diamond.

Introduction

It was shown in [1] that on the basis of an effective potential function like the Morse potential given as

$$V_{\text{Morse}} = \varepsilon\left[e^{-2p(r-r_0)} - 2e^{-p(r-r_0)}\right] \tag{1.1}$$

a contact problem can be evaluated using the mechanical parameters derived from such a potential. Here p, ε, σ are material parameters and r_0 usually denotes the equilibrium bond length. In such a case the potential would define the pair interaction. Here however, as in [1], we will apply the potential as an effective one with r_0 denoting the lattice constant (see also [2]). With respect to molecular dynamic simulation such an effective potential could be the basis for the extraction of the necessary pair and higher order interactions as demonstrated in [2]. For our feasibility study however, we will not need this, because we are only interested in the mechanical constants, especially the Young's modulus, as a function of the hydrostatic pressure P. Having this one can apply the method described in [1] to simulate a mechanical contact problem taking the pressure dependency of the Young's modulus into account.

Theory

As shown in [1] the pressure P and bulk modulus B can be derived from an effective potential. Thereby it is convenient to express P and B in units of B_0 (B at P=0) and by substituting the lattice distance r by $r=c*r_0$ result in the relations:

$$P/B_0 = \frac{e^{r_0p(1-c)}}{r_0pc^2}\left[1-e^{r_0p(1-c)}\right]; \quad B/B_0 = \frac{e^{r_0p(1-c)}}{r_0pc^2}\left[2(1+r_0pc)e^{r_0p(1-c)} - 2 - r_0pc\right] \tag{1.2}$$

We also take as estimates for the critical r leading to decomposition (c.f. [1]) the following expressions which have to be solved numerically ($r_{00} = p*r_0$):

$$6(1+c_m r_{00}) - 3e^{r_{00}(c_m-1)}(2+c_m r_{00}) = 0 \tag{1.3}$$

to extract the critical c-value c_m for maximum P(c).

As a purely mathematically based measure for the critical bond length or in our case of an effective potential the lattice distance, the inflexion point for $c_{ifp}>c_m$ could be used. This can be numerically obtained for the Morse potential via:

$$6 + c_{ifp} r_{00}\left(4 + c_{ifp} r_{00}\right) - 2e^{r_{00}(1-c_{ifp})}\left(3 + 2c_{ifp} r_{00}\left(2 + c_{ifp} r_{00}\right)\right) = 0 \tag{1.4}$$

Results

An approximate discussion with first order results for the governing nonlinear PDE

In favor of an as high as possible hardness we extract the smallest possible lattice constant from the material structures of the supposedly ultra-hard nano-composite TiN/a-Si_3N_4 and nano-composite TiN/a-Si_3N_4/$TiSi_2$ as given in [3]. We find something between 0.3714nm in a very tiny distorted region of the lattice and 0.4486nm as the average, which is - as we want to point out again, a minimum estimate clearly in favor of a maximum hardness result. Thus, the value of 0.3714nm is not really a

lattice constant, but just the two smallest bond lengths within the system described in [3] being added up while a true realistic effective lattice constant surely must be much higher. For comparison, the lattice constant of diamond is 0.3576nm. Now again in favor of a highest as possible hardness we extract from the decomposition strain ε=0.1487 for the nano-composite TiN/a-Si_3N_4 and nano-composite TiN/a-Si_3N_4/$TiSi_2$ given in [3] the highest possible value for the decay factor p as to be $2.151*10^4$ μm^{-1} (for diamond $p=0.963*10^4$ μm^{-1}). This was evaluated using the inflexion point decomposition estimate (1.4). From this we can derive a linear approximation for the pressure dependent Young's modulus $E(P)=E_0+b*P$ with b=7.3 (Fig. 1) of the supposedly ultra-hard materials simulated by Vepřek and Co. [3].

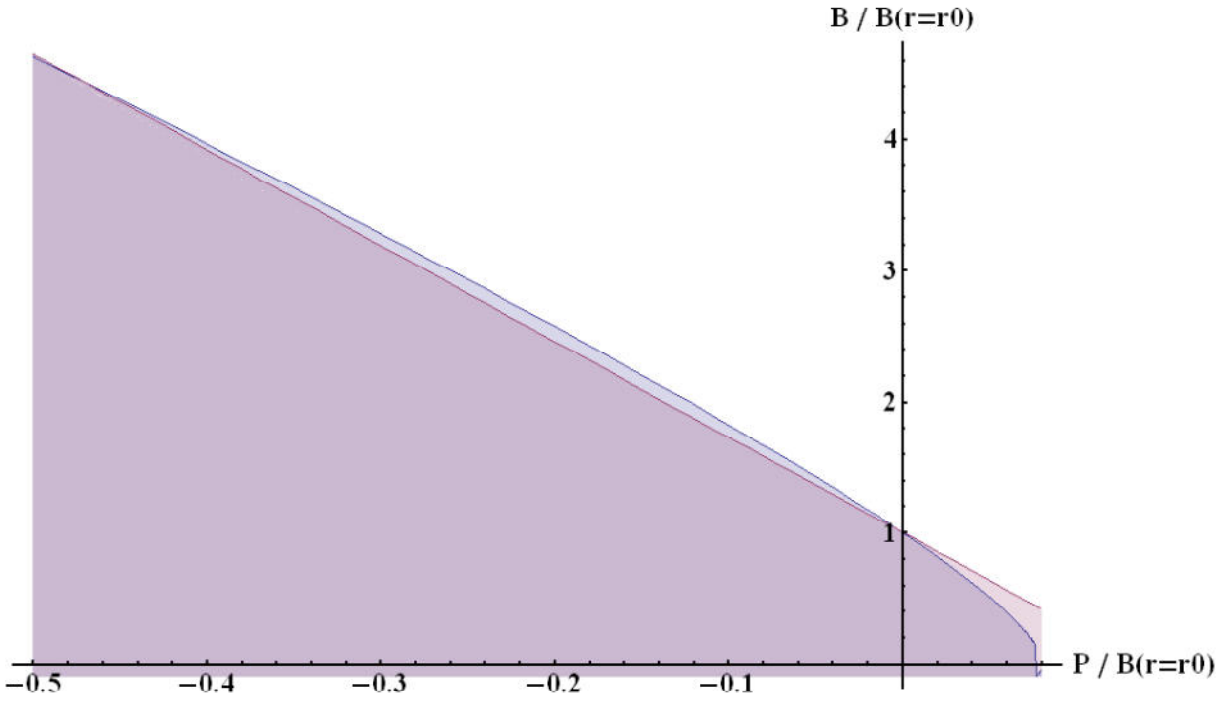

Fig. 1: Bulk modulus as function of the hydrostatic pressure evaluated from (1.2) and linear fit for supposed ultra-hard nano-composite TiN/a-Si_3N_4 and nano-composite TiN/a-Si_3N_4/$TiSi_2$ with a parameter choice in favor of a highest as possible hardness. It must be pointed out however, that this choice of parameters is rather unphysical.

We need to point out that this is a extreme choice, which is rather likely to be completely invalid if compared with the real world, but in favor of a high as possible hardness, we will use this huge b for our further evaluations. For this worst case estimate we used E_0=450GPa and a Poisson's ratio of 0.25.

With respect to the evaluation of the pressure dependent Young's modulus we have made use of the following relations between Poisson's ratio v, bulk modulus B and Young's modulus E:

$$B = \frac{E}{3(1-2\nu)} \tag{1.5}$$

As the pressure dependency of the Poisson's ratio is suspected to be negligible (e.g. [4]) we can directly give the pressure dependency for the Young's modulus. In the case of our effective Morse potential the ratios E/B_0 and E/E_0 are:

$$\begin{aligned} E/B_0 &= 3(1-2\nu)\frac{e^{r_0 p(1-c)}}{r_0 p c^2}\left[2(1+r_0 p c)e^{r_0 p(1-c)} - 2 - r_0 p c\right] \\ E/E_0 &= \frac{e^{r_0 p(1-c)}}{r_0 p c^2}\left[2(1+r_0 p c)e^{r_0 p(1-c)} - 2 - r_0 p c\right] \end{aligned} \quad . \tag{1.6}$$

Now we follow the procedure as described in [1] section entitled "Effect on resulting Young's modulus within nanoindentation experiments". Again, in favor of a hardness as high as possible, we assume a maximum effective "tip sharpening" as described in [1]. We find that in order to obtain a hardness higher than 100GPa the pressure free yield strength Y_0 must be above 40GPa. This might be considered as somehow possible, but taking the very unphysical assumption leading us to the value for b=7.3 the author expresses severe doubts about this to be realistic[1]. What is more, the stiffening effect also leads to a much sharper von Mises stress profile (c.f. fig. 8 in [1]) coming with much higher von Mises gradients. The plastic flow in the isotropic case follows these gradients in negative direction. However, with such bigger absolute gradient values pointing rather dramatically towards the contact rim the material will flows with much higher ferocity towards the contact rim leading to more flattened pressure distributions and bigger contact radii at least partially making up for the smaller (sharper) contact situation coming out from the pure non-linear elastic evaluation. This is just a hypothesis, but it directly follows from the rule of plastic flow following the negative gradient of the von Mises stress distribution.
In other words: The nonlinear stiffening produces higher negative von Mises gradients, which is producing higher flow rates towards contact rim which increases the contact radius in the elastic-plastic case and compensates for the sharpened contact as it would follow from a pure non-linear elastic prediction alone. Thus, it seems, the plasticity brings everything "back to normal" with respect to the classical nanoindentation analysis, especially with complete plastic zones being produced. Thus, the effect of higher hardness resulting from the pressure dependent Young's modulus is very likely to be diminished if not compensated for in the case of elastic-plastic indentation experiments.

A more reasonable estimate for the decay factor appears when we use (1.3) for the evaluation of the critical decomposition strain, namely $p=0.921*10^4$ μm^{-1} making the material in fact rather diamond like (for diamond we have $p=0.963*10^4$ μm^{-1}). The resulting much more reasonable b would then become b=3.8 as shown in fig. 2.

[1] It must be pointed out here, that such hardness could only be obtained if - and only if - the contact radius was measured in addition and independently from the penetration depth and load. Such a measurement system is not available now respectively has not been available for Vepřek and Co when obtaining their results (e.g. in [3]). Without such additional direct measurement feature of the contact area and by resorting to the classical nano-indentation analysis a b-parameter exceeding 20 (c.f. [1], fig. 10) would be necessary in order to show such high ultra-hardness values as reported in [3].

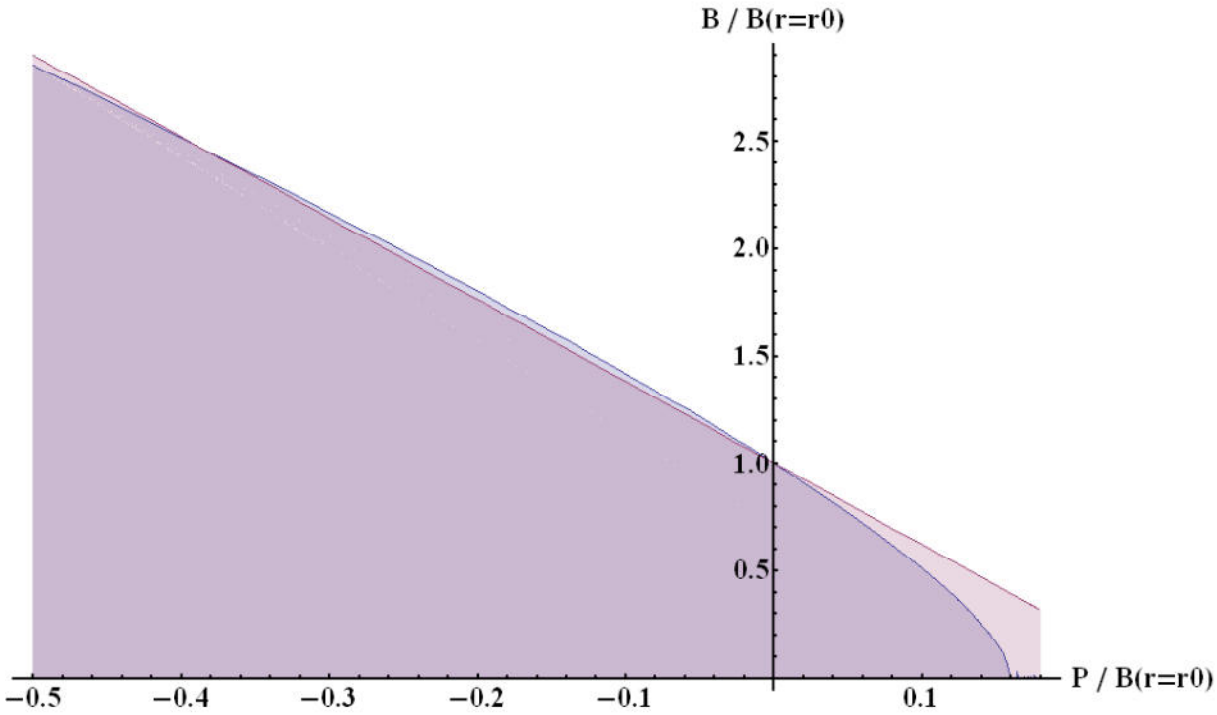

Fig. 2: Bulk modulus as function of the hydrostatic pressure evaluated from (1.2) and linear fit for supposed ultra-hard nano-composite TiN/a-Si_3N_4 and nano-composite TiN/a-Si_3N_4/$TiSi_2$ with a much more reasonable parameter choice.

We assume an effective indenter to have formed as a result of the plastic surface form change after loading a surface with a perfect cone of 70.3°. The effective indenter shall be of the shape $Z(r)=r^2/2R$ with R=2µm. Figure 3 shows the first stress invariant (equal to three times the hydrostatic stress) for a contact situation of a diamond paraboloid pressing into our supposedly ultra hard material with a load of F=50mN. Applying the linear expression for $B(P)=B_0+b*P$ using the parameter b=3.8, one can evaluate - as a first approximation directly derived from the linear homogeneous solution - the Young's modulus distribution under the indenter. As equilibrium values for Young's modulus and Poisson's ratio we use 450 GPa and 0.25, respectively (for indenter 1141 GPa and 0.07 with b=3.8).

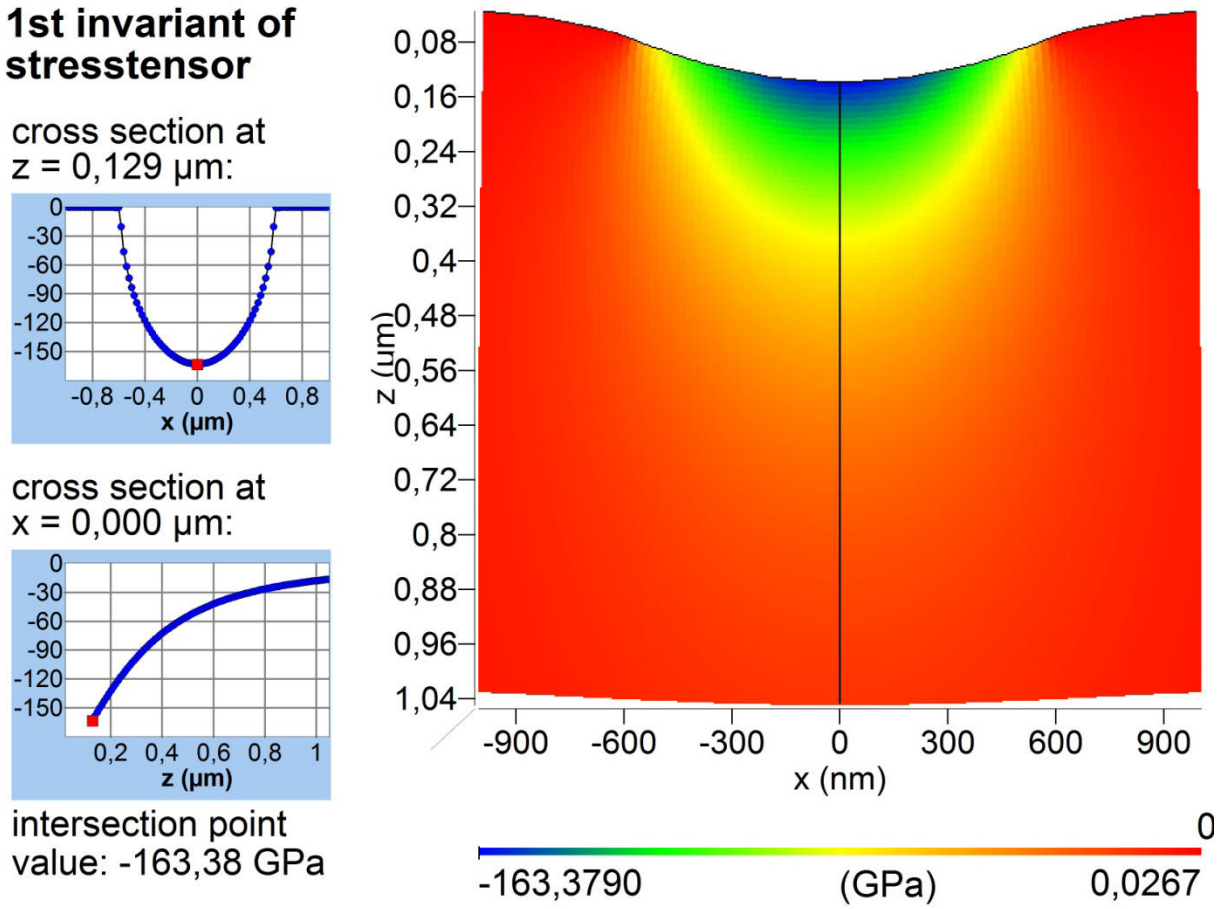

Fig. 3: First invariant stress for a fictive unloading situation (beginning of unloading) for a supposed ultra-hard material with yield strength short below 42 GPa. Boundary conditions see text.

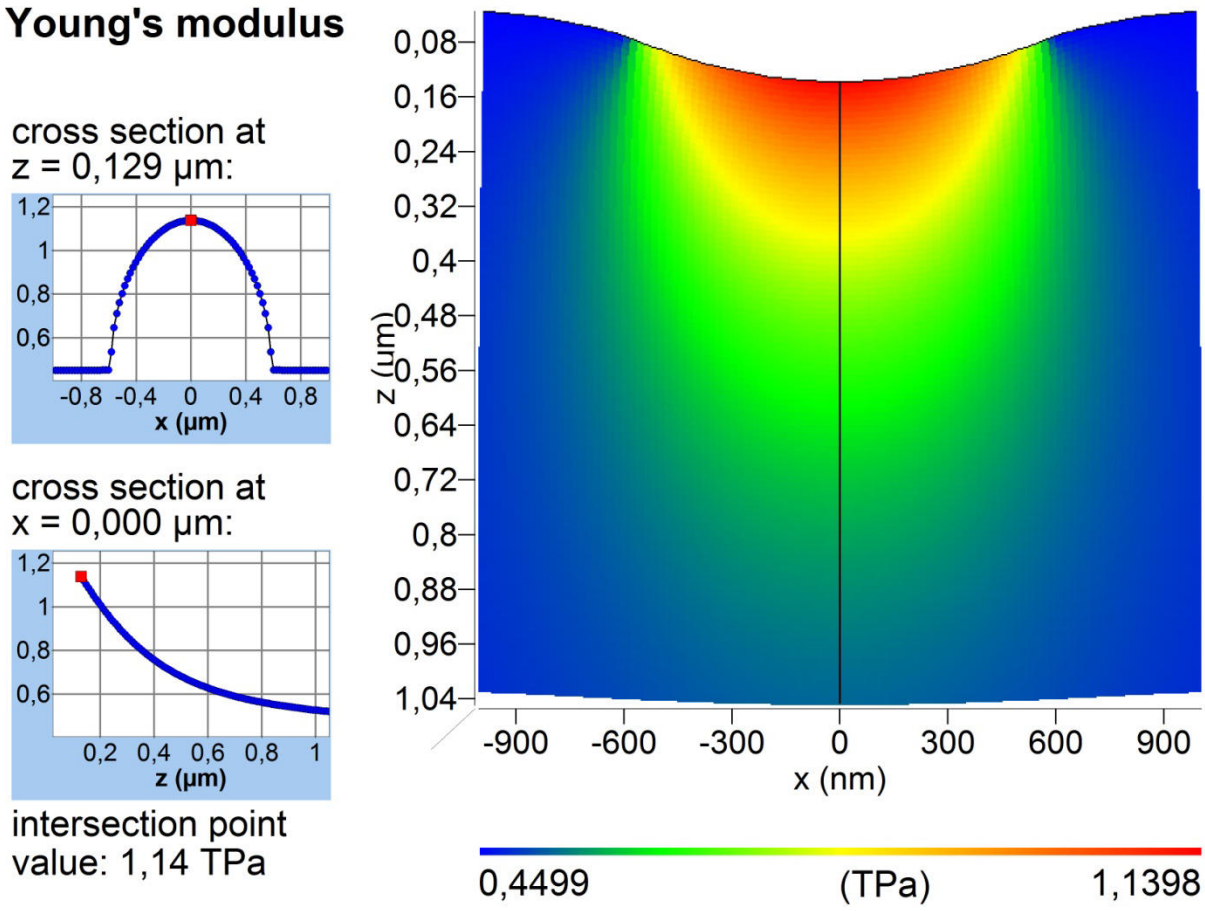

Fig. 4: Distribution of Young's modulus as result of hydrostatic stress underneath the indenter. Boundary conditions see text.

Fig. 4 shows the resulting Young's modulus profile directly following from the pressure profile given in fig. 3 taking the results presented above. We see, that in fact a significant change of Young's modulus can be observed underneath the indenter. By weighting the obtained Young's modulus distribution with displacement in z-direction of the homogeneous solution one can obtain a first estimate for the effective Young's modulus being measurable underneath the indenter at maximum load. We obtain from

$$E^{eff} = \frac{2\pi\int_V E(r,z) * w(r,z)\, r\,dr\,dz}{2\pi\int_V w(r,z)\, r\,dr\,dz} \tag{1.7}$$

for the example above E^{eff} = 636.6 GPa, which in fact is significantly higher than the equilibrium pressure free value of E=450 GPa. We explicitly point out that the yield strength of about Y=42GPa refers to the unstressed state P=0 and thus should be denoted Y_0. By also taking into account the pressure induced change of the Young's modulus in the indenter we can effectively take the "stiffening" into account by introducing a geometrically adapted contact situation of the following kind [1]:

$$Z^{eff}(r) = Z(r) - c * \sigma_{ll}(r, z = 0) \tag{1.8}$$

defining a changed effective indenter with shape Z^{eff} with a constant c yet to be determined. We need to emphasize that there are also effective indenter shapes, like the one for a flat punch with rounded edges, which cannot sharpen (c.f. [1]). For example, it was derived that with respect to a indenter of shape $Z(r)=Br^n$ with n>3 this is already the case. However, regarding the ultra hardness examples considered here it was always stated that these experiments have been dominated by the elastic response and reevaluation brought n<3. Thus, we can ignore the discussion about flat effective indenters here, especially as this would lead to even more arguments against ultra-hardness (for more, the reader is referred to [1]).

In favor of a very high hardness we now assume c such that it fully compensates for the pressure induced stiffening with respect to the measured penetration depth as been elaborated in [1]. Taking into account, that the hardness is the projected area of the contact and assuming a mathematically sharp cone of 70.3° a fictive hardness of 81.2 GPa would be evaluated for the contact situation given above.

Another calculation with an assumed yield strength of 50.4 GPa results in a hardness of impressive 109.4GPa.

The question we want to answer now is whether the results shown here do support the discussed ultra-hardness (H>100GPa) results reported to be obtained for nanocomposite coating materials like nc-TiN/a-Si_3N_4 or nc-TiN/a-Si_3N_4/$TiSi_2$ (e.g. [5] and for the discussion see e.g. [7]).

At first it should be made clear here however, that without taking the effect of "stiffening" into account no such high hardness results can be obtained at all. Any classical analysis like the Oliver and Pharr method for nanoindentation would not take the stiffening and subsequent surface effective form change into account and thus would not give such high values. For our two examples given above the "experimental" findings would have to be 45 GPa and about 53 GPa instead of 81.2 GPa and 109.4 GPa.

However, in principle and by taking the "stiffening" into account ultra hardness above 80 GPa seems to be possible if a yield strength of well above 40GPa is present. In [3] Vepřek and co-workers gave the theoretically possible yield strength as Y=2.24*(12 to 32) GPa, with the factor 2.24 coming from the Sachs averaging for randomly oriented crystals [6]. It should be noted however, that this averaging ignores any possibly weaker grain boundaries. Nevertheless, the apparent possible yield strength of Y=(26.88 to 81.68) GPa seem to allow hardness exceeding 100 GPa.

The author however, taking the values of theoretical strength up to 32 GPa to be correctly obtained from first principle evaluations by Vepřek and coworkers, doubts the applicability of the Sachs averaging due to the disregard of the grain boundary effect, defects or any other weaker part within the material.

Interestingly, even a Y=81.68 GPa would only result in a hardness of about 85 GPa maximum if analyzed classically without any stiffening taken into account or workhardening or other strengthening effects assumed. This can be derived from a Hertzian contact model assuming a paraboloid of r^2-shape giving the elastic-plastic surface during unloading for any sharp indenter. For any other reasonable effective surface shape the hardness would be even smaller. And as described above, the "sharpened" von Mises stress profile will probably lead to a more pronounced plastic flow towards the contact rim leading to flattened normal stress profiles which is equivalent to effective

indenter shapes of r^n with n>>2. This however, decreases the measurable hardness rather dramatically.

Last but not least, following a hint of A. Fischer-Cripps (s. acknowledgments), there is a principle limit for the hardness one could measure with a Vickers or Berkowich indenter tip as presented in equation (34) in [8]. From the formula given in [8] a limit for our material in question of a hardness of about 60.6 GPa can be extracted. However, as this formula is based on the flat surfaced half space theory and thus contains the true contact area we derive about 68.7 GPa as the measurable hardness limit by taking the projected contact area for Vickers, Berkowich and effective cone of half angle 70.3°. With the stiffening or sharpening effect taken into account, this value is not valid anymore, and thus, using an indentation analysis method which fully accounts for the non-linear pressure dependent Young's modulus higher hardnesses would be measurable than the limit given about would set. But by no means this is possible with classical indentation analysis, except in the case of severe flaws in measurement set up or analysis.

An Approximation free approach based on the law of energy conservation

In order to find an approach were we do not need to resort to an approximation of the governing partial differential equation of elasticity being nonlinear due to a pressure dependent Young's modulus we now apply a simple comparison with diamond. For this, we assume that the energy being stored in the elastic part of any indent must be taken on by the atomic interaction potentials of the atomic structure residing underneath the contact zone respectively under and around the same. We see immediately that this is just the energy conservation law we are going to use here. At first we evaluate the total energy of the elastic contact problem and combine it with the usual fitting approach for indentation load depth curves, which is

$$F = C \cdot (h - h_0)^m \tag{1.9}$$

with F, h and h_0 denoting load, depth and residual depth, respectively and C and m being fitting parameters. The result is

$$\begin{aligned} E_{tot} &= \int_0^{h_{el\_tot}} F(h)dh_{el} = \int_0^{h_{el\_tot}} C \cdot (h - h_0)^m dh_{el} \\ &= \int_0^{h_{el\_tot}} C \cdot {h_{el}}^m dh_{el} = C\frac{h_{el\_tot}^{m+1}}{1+m} \end{aligned} \tag{1.10}$$

Now, as already stated above, this total energy must be distributed among the atomic interactions potentials under and around the contact. So we have

$$E_{tot} = \sum_{\forall i} \left[V_i(r_i) - V_i(r_{0i}) \right] \tag{1.11}$$

As an example we now use the results for a "ultra-hard coating" with claimed hardness of 113.2 GPa [9]. Reanalyzing of the load-depth data for the indentation in question as obtained from one of the authors of [7] and correcting for the coating structure (6µm coating on steel) as reported in [9] the resulting true coating Young's modulus is about 484 GPa. With respect to the coating correction the reader has to be referred to the literature (e.g. [10 - 13]) as an elaboration of the method would go too far here. The original Young's modulus claimed for this coating by the means of the same data

was 698 GPa [9]. It has been shown in [14] and [7] however, that even without the coating correction applied here, the correct result for the Young's modulus must lay well below 500 GPa (431,5 GPa with classical power-law fit as performed by the author, but see also [7] and [14] for comparison). Thus, the 698 GPa claimed by Vepřek and co-workers are a relatively doubtful result already. But here we want to concentrate on the hardness of claimed 113.2 GPa. By the means of [12] we can also evaluate the yield strength from the indentation data and find it to be around 48.6 GPa, while the coating hardness was found to be 64 GPa. This is rather far away from the claimed 113.2 GPa in [9] and so we want to investigate the principle physical feasibility of such a result in trying to find a potential interaction allowing such a hardness to come true in reality.

In order to avoid any linearization or other kinds of approximation with respect to the interaction this time we resort to just comparing the potential of diamond with the one of a hypothetic ultra-hard material both satisfying the law of energy conservation as given above. It is absolute plausible to say that any indent with just F and h being measured could be simulated by a number N of interacting atoms with Potentials V(r). Averaging over all potentials one might even give just one effective potential, named V_{eff}. This gives us

$$\bar{V}_{eff} = \frac{E_{tot}}{N} = \frac{\sum_{\forall i}\left[V_i(r_i) - V_i(r_{0i})\right]}{N} \tag{1.12}$$

With i running from 1 to N. This way we are back to the original potential structure except for the average character this time. Now we only need to obtain a reasonable number for N for any given contact situation. The contact situation we are considering is the one leading to the claimed ultra-hardness of 113.2 GPa as presented in [9]. Here F was 70mN. The number of atoms which interactions are contributing to the total elastic response during unloading must be proportional to the volume being elastically strained and thus proportional (somehow) to contact radius a or contact area A, which we can easily obtain from the definition of Hardness H=F/A. We also need to take into account however, the density of atoms respectively potentials being inversely proportional to the lattice constant or our, be it real or effective, r_0^3. In order to avoid any guesswork about the real number of N, we simply concentrate here on comparing the ultra-hardness potential with diamond. This appears as a rather reasonable thing to do, because both materials are supposed to have similar strength. Any structural difference of the two will be considered and discussed later. This directly brings us to the following relation

$$\frac{V_{Diamond}}{N_{Diamond}} = \frac{V_{UH}}{N_{UH}} \tag{1.13}$$

with the number $N_{material}$ (material = "Diamond", "ultra-hard material") standing for number of contributing interactions in the contact field volume v_c been proportional to

$$N_{material} \sim \frac{v_c}{r_0^3} \sim \frac{\sqrt{A^3}}{r_0^3} \tag{1.14}$$

leading to

$$\frac{V_{Diamond} \cdot r_{0\_UH}^3}{\sqrt{A_{Diamond}^3}} = \frac{V_{UH} \cdot r_{0\_UH}^3}{\sqrt{A_{UH}^3}} \tag{1.15}$$

and thus[2]:

$$V_{Diamond} = \sqrt{\left[\frac{H_{UH}}{H_{Diamond}}\right]^3} \cdot \left(\frac{r_{0\_UH}}{r_{0\_Diamond}}\right)^3 \cdot V_{UH} \tag{1.16}$$

Setting $H_{Diamond}$=100 GPa, $r_{0\_Diamond}$=0.3576 nm, H_{UH}=113.2 GPa we have now to find a potential V_{UH} satisfying the equation (1.16). Thereby we need to take into account however, that this potential also depends on r_{0_UH}, s. eq. (1.1). The potential parameters for diamond (p and ε) are taken from [2] with respect to ε and from

$$p = \frac{3}{4}\sqrt{\frac{B_0\, r_0}{\varepsilon}} \tag{1.17}$$

with respect to p. There we will use the parameters usually applied in indentation analysis, which are 1141 GPa for the Young's modulus and 0.07 for the Poisson's ratio and result in $p_{Diamond}$=0.86691. We also set the Poisson's ratio for the ultra hard material to 0.2 and use our fit result mentioned above for the Young's modulus, which was E=484 GPa.

Now, the first interesting finding is that there is no physical meaningful solution to equation (1.16) for any r_{0_UH}>0.39nm, which completely rules out the average lattice distance as it was found by Vepřek and co. (e.g. in [3]) being about 0.4486nm. Even a very low and already completely impossible r_{0_UH}=0.38nm (note well: this must be the average of a mesoscopicly big contact region and we have $r_{0\_Diamond}$=0.3576nm for comparison) would require a potential depth greater than that of diamond (c.f. figure 5).

[2] The author is aware of the fact that differentiation of V with respect to the normal direction would allow to correlate the indentation experiment even more directly with the potential. However, as the results coming out from such an approach are even less supporting the "idea" of ultra-hardness we are not considering this option here.

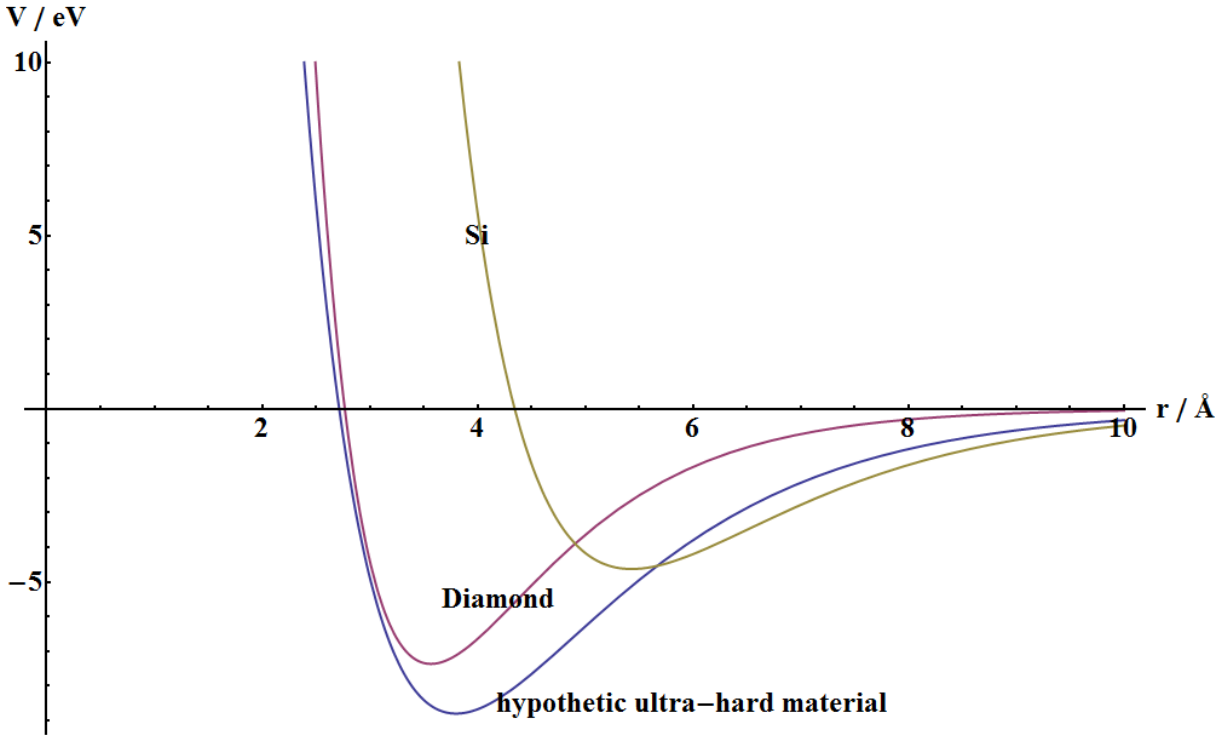

Fig. 5: Potential for Diamond, Silicon and a rather impossible hypothetic ultra-hard material.

Of course, this survey might not be called complete and thus, we will not claim to have theoretically shown that ultra-hardness is not feasible, but currently we simply see no plausible way to compose an earth-bound material under the boundary conditions given in a physically meaningful manner. The author was absolutely unable to find any reasonable potential allowing or at least partially explaining the hardness claims made by Vepřek and co-workers in [3].

Including compressive intrinsic stresses

It is well known, and thus, will not be elaborated or demonstrated here, that compressive biaxial intrinsic stresses can increase the hardness results due to postponed onset of plastic flow caused by the intrinsic stress state. In order to investigate this intrinsic stress enhancement effect we simply resort to one example with a rather extreme biaxial stress state of σ_{rr} = -10 GPa. The resulting pressure respectively first invariant stress I_1 for a biaxial stress state has to be evaluated as follows:

$$P = \frac{I_1}{3} = \frac{1}{3} \cdot \begin{pmatrix} \sigma_{rr} & 0 & 0 \\ 0 & \sigma_{rr} & 0 \\ 0 & 0 & 0 \end{pmatrix}_{ii} = \frac{2}{3} \cdot \sigma_{rr} \tag{1.18}$$

From our formula for the dependency of pressure and displacement (1.2) we can derive the necessary displacement of r = 0.992306 r_0. Figure 6 illustrates the dependency.

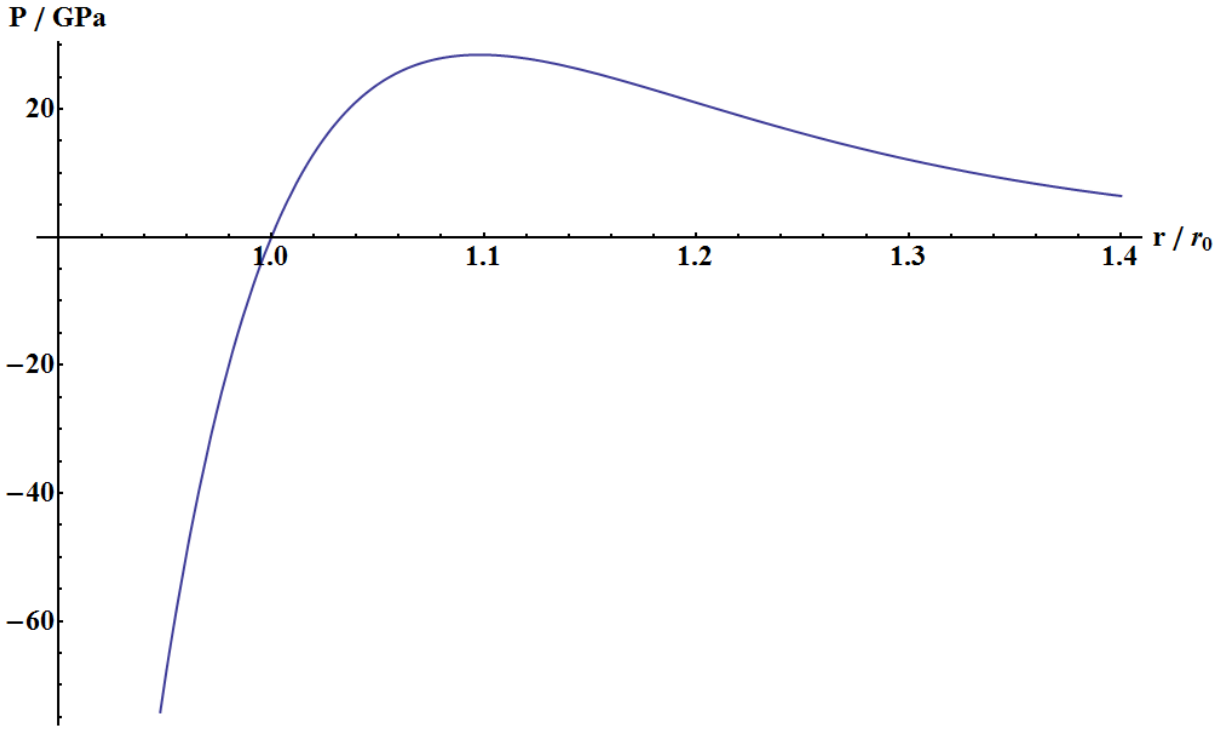

Fig. 6: Pressure as function of lattice constant over state of equilibrium for hypothetic ultra-hard material.

We now find (Fig. 7) that reasonable interaction potentials can indeed be obtained with slightly less peculiar lattice distances. Already for about 1.09 times $r_{0\_Diamond}$ we obtain a solution with an energy minimum smaller in absolute value than that of diamond (fig. 7, blue curve). Before we conclude however, that ultra-hardness could be possible under such circumstances, where biaxial stress, high particle density and a diamond-like, but distorted structure are coming together, we should remind ourselves, that the assumed biaxial stress is rather high and the necessary integral (average) atomic density for a mixture of Ti, N, Si still is within the 10%-range of that of diamond... bulk diamond one should add, while the hypothetic ultra-hard nanocomposite was supposed to be a coating.

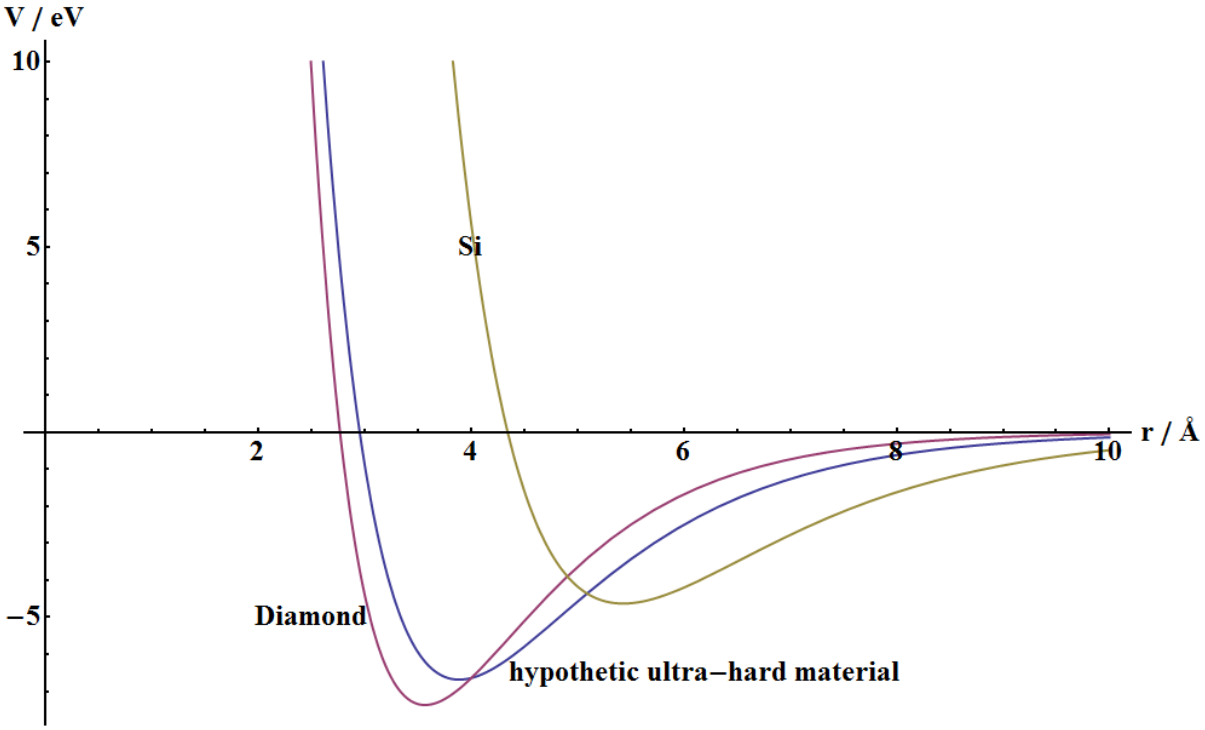

Fig. 7: Potential for Diamond, Silicon and a rather impossible hypothetic ultra-hard material with an assumed biaxial intrinsic stress of -10 GPa.

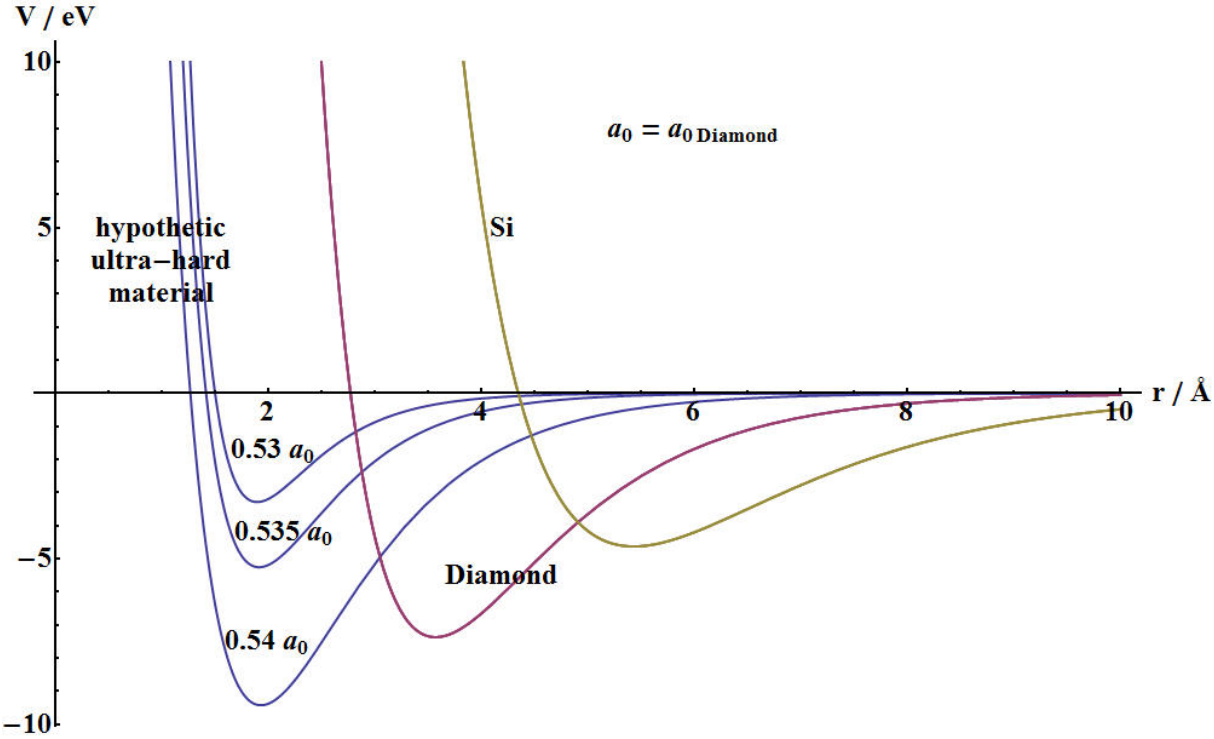

Fig. 8: Potential for Diamond, Silicon and three rather impossible hypothetic ultra-hard material with fcc-structure.

In order to investigate this a bit more closely we now assume the hypothetic ultra-hard material to be of FCC-structure as being claimed to be by Vepřek (e.g. [15]). Interestingly, now we have to go to even more extreme lattice constants in order to reach the required boundary conditions set by the claimed hardness of 113.2 GPa (fig. 8). Even with an assumed biaxial stress the situation is not getting much better as one can deduce from fig. 9.

It should be mentioned at this point that the lattice constant of the ultra-hard material was found to be around 420 pm [16].

This is, as we want to emphasize, more than double the biggest lattice constant being found here as a possible solution making the ultra-hardness results of Vepřek and co-workers at least theoretically feasible (assumed perfect crystal structure with no lesser dens regions anywhere in the whole coating).

Now we investigate the effective potential function of a "ultra-hard-material" as found 'as at least in principle possible' in [7]. Thus, we assume a hardness of 64 GPa and find the resulting potential as shown in Fig. 10. We immediately see, that even this much lower hardness would be impossible taking the impossible lattice constant necessary which is by far too small again. We need to point out that due to the insufficient description of the experiments by Vepřek and co-workers a perfectly, mathematically sharp indenter was assumed resulting in the 64 GPa mentioned in [7] and in this work (s. above).

A hardness resulting in reasonable effective potentials is found here to be equal or below 40 GPa. The difference to the "in principle possible 64 GPa" mentioned above can easily be explained by tip rounding of the indenter used by Vepřek and co-workers (due to “daily use on hard coatings” as Vepřek himself put it in one of his many papers). To be clear, these 40 GPa are still not a bad hardness, but this is very far away from those 113.2 GPa claimed by Vepřek and co-workers. Those 40 GPa we found for their coatings however, are nothing out of the ordinary.

This makes the claims made by Vepřek and co-workers not only rather unbelievable but also almost embarrassing. The latter attribute must unfortunately also be given to the whole review performance of all those more than hundreds of publications meanwhile being published on this subject mainly by Vepřek and co-workers. As almost all of these papers sport some acknowledgement to some national or international projects by which the work obviously was supported even more questions must be raised with respect to the quality of evaluation and subsequent results control of certain projects and the outcome of the same.

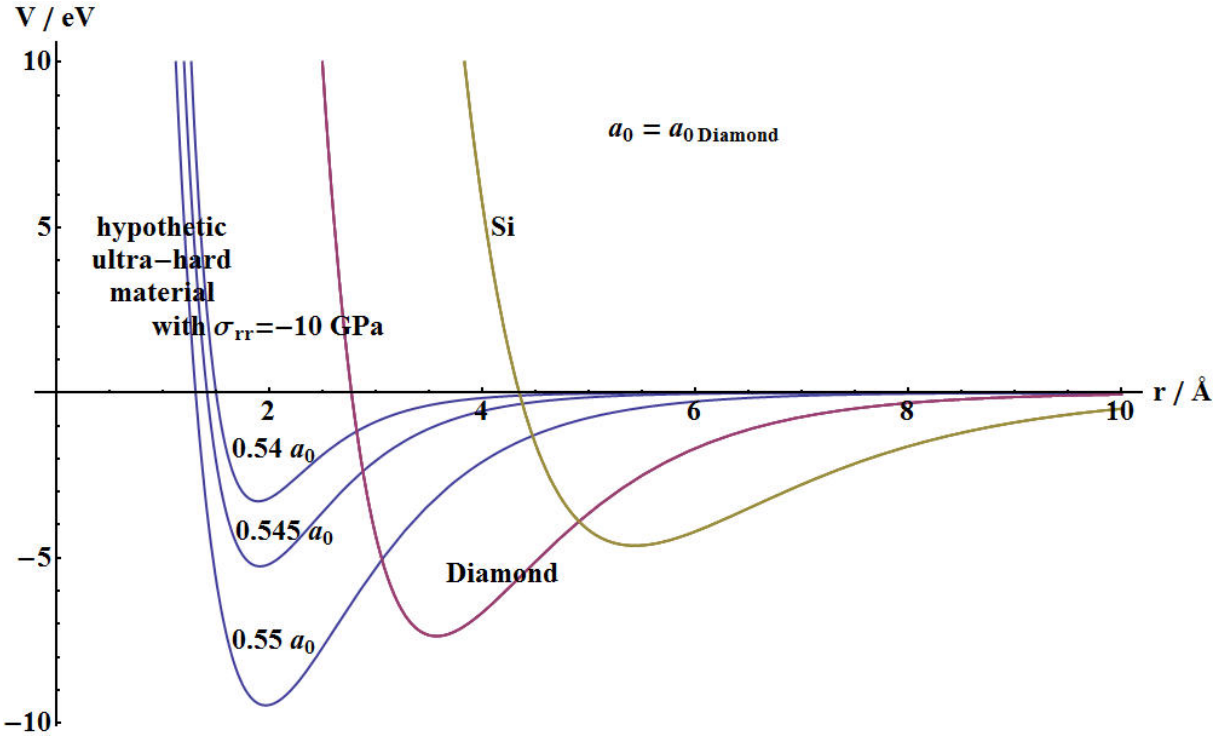

Fig. 9: Potential for Diamond, Silicon and a rather impossible hypothetic ultra-hard material with fcc-structure and an assumed biaxial intrinsic stress of -10 GPa.

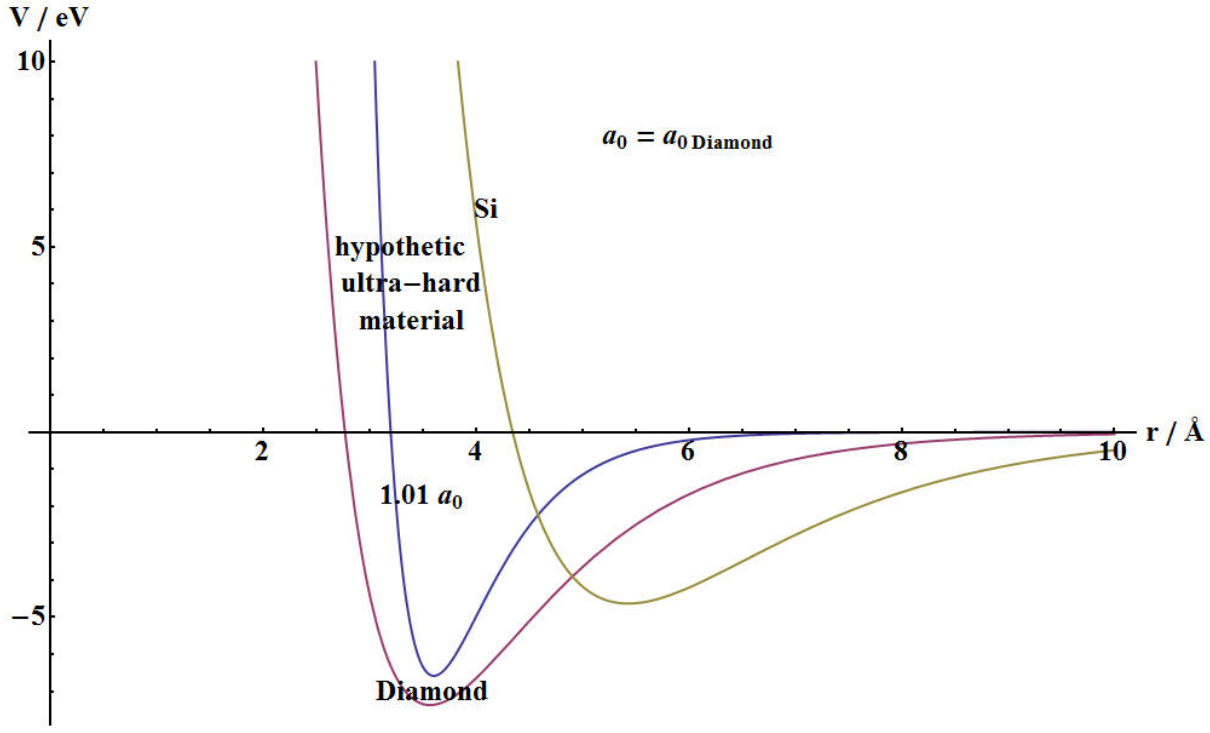

Fig. 10: Potential for Diamond, Silicon and a still very much impossible hypothetic "ultra-hard" material with fcc-structure with H=64 GPa (s. text).

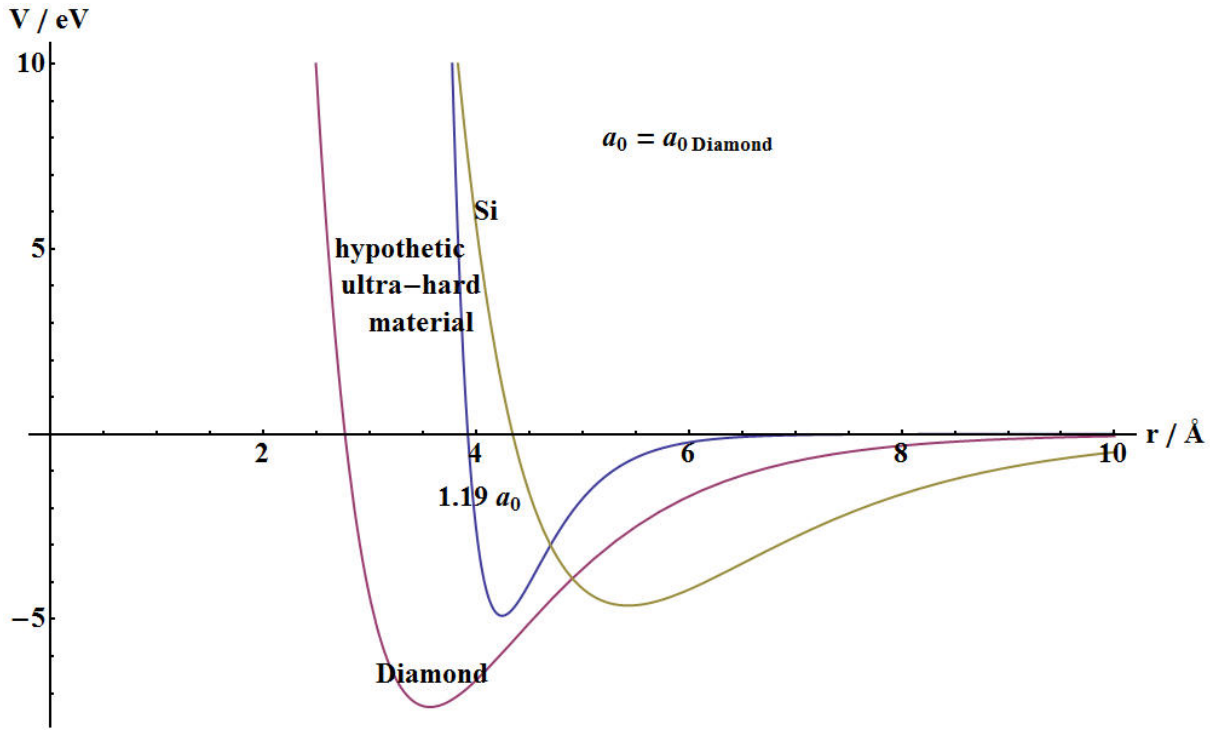

Fig. 11: Potential for Diamond, Silicon and a pretty much possible, but rather unimpressive hypothetic "ultra-hard" material with fcc-structure with H=40 GPa (s. text).

As the evaluation as outlined here is not very difficult and could also been applied to other materials in order to find their theoretical performance with respect to hardness measurements the reader might like to perform some trials with her or his own sets of parameters. The author and his partners have therefore set up a small program allowing to play around with parameters and repeating the evaluations shown here last [17].

Possible Solutions for Ultra-Hardness Applying the Energy Approach

Now we want to apply the methods developed above in order to extract "construction parameters" for possible hard ($H \geq 60GPa$), super-hard ($H \geq 80GPa$) and ultra-hard ($H \geq 100GPa$) materials. As we consider this only a rather academic investigation we will concentrate on diamond structures only. We seek the solutions as functions of the parameters lattice constant a_0, Young's modulus E and Poisson's ratio ν. Due to the non-linear equations being of need here the evaluation results some rather sensitive (almost chaotic) behavior with respect to the input parameters. Still one can obtain relatively clear limits for the possible material structure of the demanded hardness range. Figures 12 – 14 are presenting the solutions we have found.

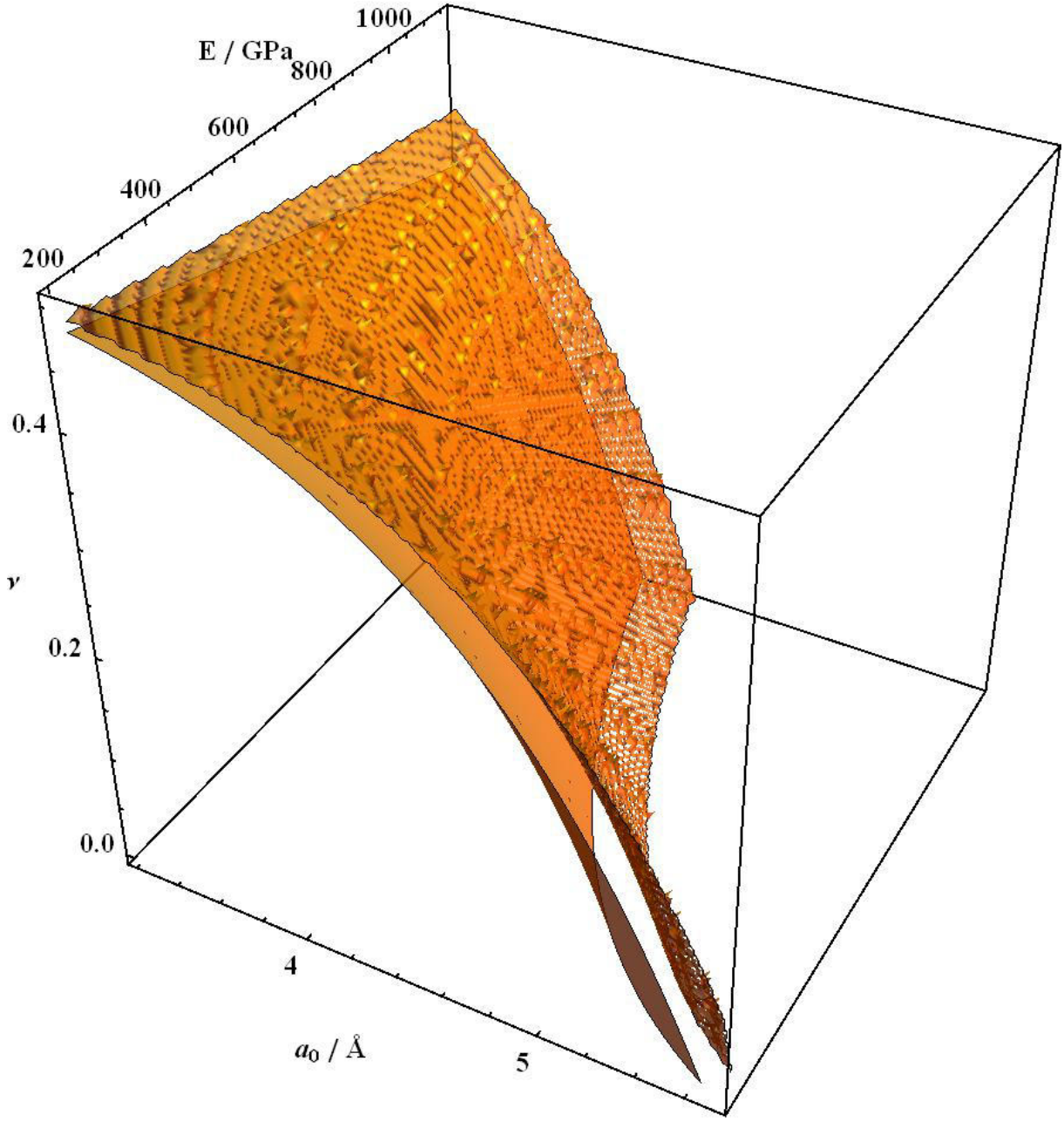

Fig. 12: Possible constructional solutions for materials with Diamond structure to reach a hardness of around 60GPa (s. text). The two surfaces are embedding "parametric solutions" for this kind of hardness.

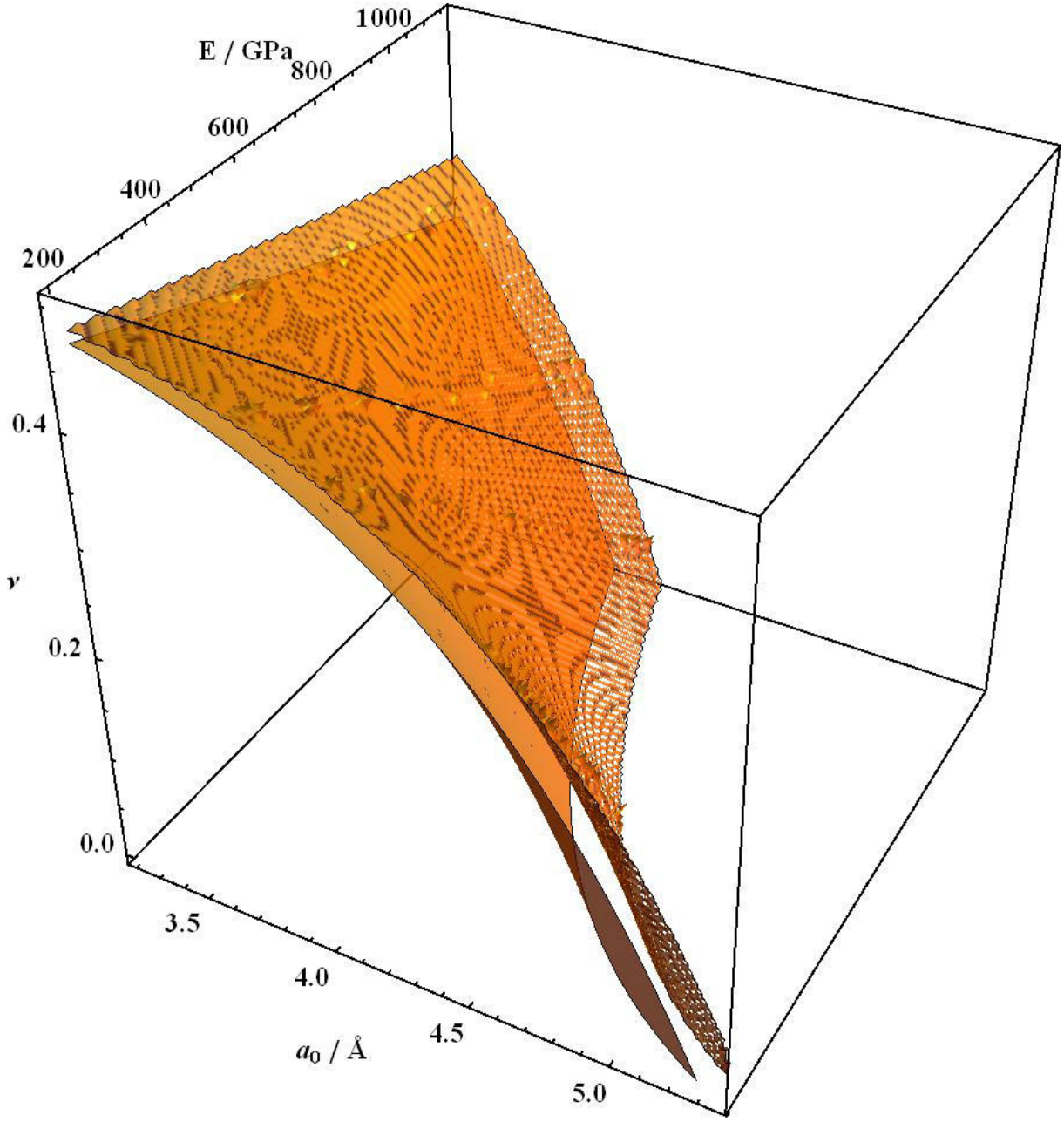

Fig. 13: Possible constructional solutions for materials with Diamond structure to reach a hardness of around 80GPa (s. text). The two surfaces are embedding "parametric solutions" for this kind of hardness.

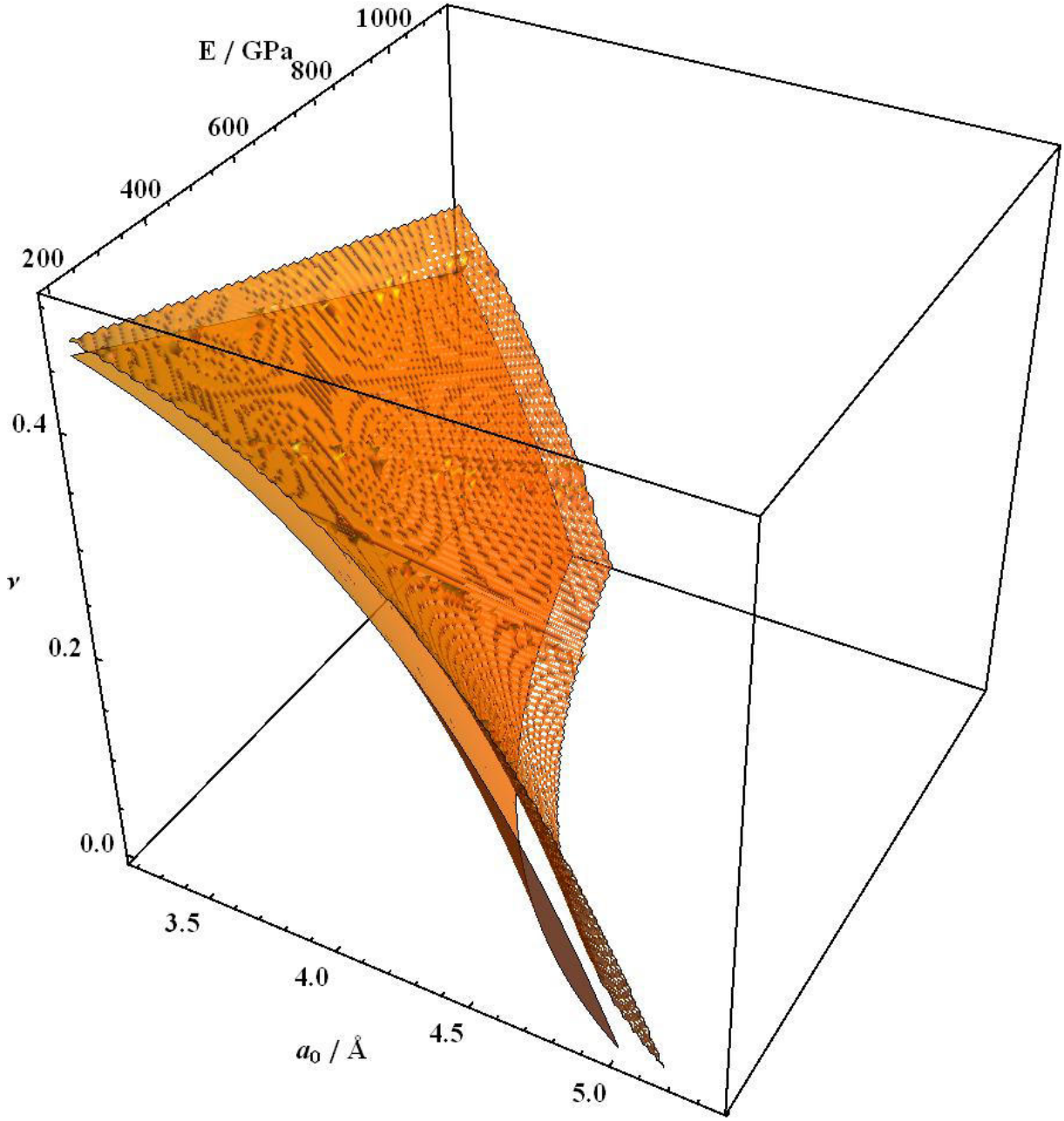

Fig. 14: Possible constructional solutions for materials with Diamond structure to reach a hardness of around 100GPa (s. text). The two surfaces are embedding "parametric solutions" for this kind of hardness.

Conclusions

Taking the results of Vepřek and coworkers about the theoretical strength of nc-TiN/a-Si_3N_4 or nc-TiN/a-Si_3N_4/$TiSi_2$ it seems impossible to measure hardness higher than 65 GPa using classical analysis methods (like Oliver and Pharr). However, taking the pressure induced Young's modulus and yield strength into account and using such a non-standard analysis method as shown here hardness above 100 GPa are possible for yield strength values above 47 GPa. Only if workhardening or other rather mysterious strengthening effects would take place during indentation also the classical analysis could

show such high values. But this can happen only if also the highest possible strength (32 GPa) and the Sachs averaging are correct, which is rather doubtful because the latter ignores any grain boundary effects. On the other side however, the author was completely unable to find any reasonable atomic interaction potential allowing such high hardnesses in the first place.

In summery the author has to conclude,

either the ultra-hardness results reported in [5] are incorrectly measured or analyzed or both and the theoretical results apparently proving the possibility of hardness >100 GPa [3] are flawed or

this study is inappropriate or incomplete or both.

The maximum hardness the author can make out for those supposedly ultra-hard Vepřek-coatings taking the means described here is equal or even below 40 GPa.

The reader is therefore motivated to repeat the evaluations made here, perhaps even extend the search radius and report any findings leading to better models and / or ultra-hard results. A small software package has been set up for exactly this reason [17].

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