Silicon nanoindentation modelled by hybrid potential

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Abstract

The aim of molecular dynamics is to examine and predict structure-dependent properties of physical systems by means of a reliable model of atomic interactions. However, when none of the applied models mirrors a system’s behaviour of interest, developing a suitable one from scratch becomes a necessity. It is a complex and time-consuming process, but here we use a simple alternative: it is to merge already existing - yet operationally diverse - potentials into a single one. We demonstrated this approach by combining Tersoff and Stillinger-Weber potentials into hybrid one that makes it possible to reflect an intricate process of nanoindentation of silicon, which none of the currently available potentials is able to do on its own. Molecular dynamics simulations with an hybrid potential reflected the subsequent stages of Si nanodeformation: the transformation diamond cubic (Si-I) to the $\beta$-tin (Si-II) phase, the formation of the r8 (Si-XII) structure as deformation proceeds, and finally the nucleation of dislocations.

Keywords: molecular dynamics simulations, silicon, interatomic potential, phase transformation, dislocations

1. Introduction

Modern materials science owes much of its success to computer simulations \cite{1, 2}, which examine and predict a vast array of phenomena. Materials physics has no shortage of “ready-made” potentials at its disposal. Their limited transferability means that one process is usually modelled at the expense of another, thus precluding the interplay of key phenomena. Moreover, building an appropriate interaction potential is not easy as it usually involves a trade-off between accuracy and consumption of computational resources.

The molecular dynamics (MD) simulation method accounts for the interatomic forces in terms of the gradient of the potential energy function in conjunction with a set of adjustable parameters to reflect the specific conduct of a modelled system. Thus, a careful consideration of the available interatomic potentials must precede any MD simulations. However, when none of the applied potentials mirrors a system’s behaviour of interest, developing a suitable one from scratch becomes a necessity. It is a complex and time-consuming trial and error process, but our article refreshes a simple and promising alternative: it is to merge two already existing - yet operationally diverse - potentials into a single one. This new, hybrid potential - by combining the unique characteristics of its components - makes it possible to simulate some crucial, coexisting features of a system under examination. Using this approach, we have been able to carry out a simulation of the intricate process of nanoindentation of silicon, which is rather ambiguous with the currently available potentials.

Silicon remains the iconic semiconductor of modern technology. Recent applications include surface acoustic wave photonic devices \cite{3}, light sources \cite{4} or atomic scale instruments and memories \cite{5}, to name but a few. So after decades of research, it would seem that every property of this important material has been investigated \cite{6}, but matters such as nanoscale deformation of silicon crystal and its incipient plasticity, in particular, are far from being fully understood. Numerous nanoindentation experiments combined with microscopic observations demonstrate that, under increasing straining, the initial Si-I structure undergoes a series of transformations to the high-pressure Si-II, Si-III (bc8), Si-XII phases \cite{7–15}. This, however, would not be the full picture as it disregards the presence of numerous dislocations, slip bands and cracks in the vicinity of the acting indenter tip \cite{11, 12, 16–18}. Thus, a microscopic examination of the Si structure nano-deformed under a spherical tip by Wong et al. \cite{10–14} led them to the conclusion that phase transformation and defects generation were “competing deformation mechanisms, with one or the other process initiating plastic deformation under particular loading conditions”. Focusing for a moment on other semiconductors, it is worth noting that the nanoindentation-induced elastic-plastic transition in GaAs crystal is initiated by the phase transformation \cite{19–21}, while nanoscale plasticity in GaN is exclusively governed by the activity of dislocations \cite{22, 23}.

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There are two distinct mechanisms of silicon’s incipient plasticity at work here: the first assumes the dominant role of phase transformation followed by dislocations activity, while in the second, plasticity starts with the nucleation of defects followed by subsequent phase transformations. Regardless of which scenario unfolds in reality, none of the currently available potentials meets the requirement of accurately modelling a complex nanoindentation process, since each one of them suffers either from limited transferability [24] or high computational-time expense. Such is the case with the interatomic potentials developed with the aid of machine learning [25, 26], which are capable of a high degree of accuracy on a par with ab initio methods. However, they exhibit such computational complexity as to render them impracticable for the purpose of nanoindentation, which requires a simultaneous consideration of multimillion atomic systems and the application of long time scales [27]. As a result, modelling of the silicon mechanical behaviour continues to rely heavily on either the Stillinger-Weber (SW) [28] or Tersoff-type [29–36] potentials. The former approach has been designed with the Si-I and amorphous phase in mind, and proves particularly efficient at capturing dislocation-based processes. By contrast, Tersoff-type potentials reflect phase transformations that occur in the diamond cubic and metallic (high-pressure) phases of silicon. It follows that neither model is versatile enough to capture the interplay between both phenomena, thus precluding proper investigation of Si crystal behaviour under localized stress. Early critical comparison of interatomic potentials for Si was provided by Balamane et al. [37] while tests performed for the case of Si lattice under large shear strain were done by Godet et al. [38].

There have been numerous efforts to modify the original Tersoff interatomic potential in order to increase its accuracy and transferability, e.g. [33]. Thus, the angular-dependent term of the Tersoff formula was revised by Kumagai et al. [35], who considerably improved the description of silicon’s elastic properties or its melting temperature. More recently, the Kumagai potential have been employed to examine nanoindentation-induced deformation of silicon [39, 40]. A significant advance in the modelling of silicon brittleness was made by Pastewka et al. [36], whose screened version of the Erhart-Albe potential (EAs) [34] manages to capture both phase transformations and dislocations activity in silicon deformed by nanoindentation [41–43]. Despite its undeniable value, the Pastewka approach results in an overestimation of the contact pressure at the onset of phase transformation, and rather poorly developed dislocation structure (see Ref. [42]).

Here we present the hybrid (H) interatomic potential simultaneously, showing that it inherits essential features of both the SW and T2 models. We also demonstrate that the hybrid potential provides a reliable account of the sequence of phase transformations and dislocation activity which contribute to the incipient plasticity of silicon.

| T2 | SW | H | T3s | Ref. |
|----|----|---|-----|------|
| $E_c$ | -4.63 | -4.34 | -4.55 | -4.55 | -4.63 | -4.62 |
| $c_{11}$ | 122 | 151 | 130 | 130 | 143 | 166 |
| $c_{12}$ | 86 | 76 | 83 | 83 | 75 | 64 |
| $c_{44}$ | 10 | 57 | 23 | 24 | 69 | 80 |
| $u_{<112>}$ | 1.84 | 3.20 | 2.22 | 2.22 | 2.20 | 1.91 [38] |

2. Methods

2.1. The hybrid potential for Si

Simulations of nanoindentation made using the T2 potential [30] are far from the reality of nanodeformed Si since they cannot account for dislocations activity. The problem is reflected by the simulation results of silicon nanospheres compression [45]. The structural changes in the nanospheres were limited only to the Si-I→Si-II phase transformation but without the dislocation activity. Surprisingly, the compressed nanospheres resembled a flattened rubber balls rather than a real object of brittle material. On the other hand, structural changes in compressed silicon nanospheres modelled by the SW [28] potential occurred exclusively with the participation of dislocations and the local amorphization of a small volume right below the indenter [46]. These two different perspectives of the phenomena occurring in the strained silicon suggested the idea of mixing the T2 and SW potentials in order to obtain a more transferable hybrid.

The solution we are offering is based on a weighted sum of the T2 and SW potentials for silicon, such that the potential energy $E_H = w_{T2}E_{T2} + w_{SW}E_{SW}$. Careful testing of variously weighted versions of the hybrid potential resulted in a unique values: $w_{T2} = 0.71875$ and $w_{SW} = 0.28125$, which we regard as close to optimal for silicon under localized stress. Although the physical arguments constituting the analytical form of the T2 and SW models differ, they can be considered as a certain cases of more general angle-dependent embedded atom method potential [47]. The purpose of supplementing the T2 potential with a small portion of the SW potential was to “stiffen” the former. This becomes clear when one recall that the SW potential formula contains a penalty function that strongly suppresses the deviation from 109.47°, the bond angle characteristic of the diamond structure. The details of potentials mixing and a method of its application can be found in Supplementary Materials.

An initial examination of the hybrid potential was performed alongside the T2, SW, and T3s (screened) models for comparison. The tests included calculations of elastic
predicts the shear modulus performed with different potentials. The hybrid potential related to differences in the course of structure relaxation et al. cell, while the stacking fault energy calculation procedure's potential energy by the number of atoms. The elastic constants were calculated applying small volumetric, tem's potential energy by the number of atoms. The elastic constants were calculated applying small volumetric, tetragonal and rhombohedral deformation to the Si supercell, while the stacking fault energy calculation procedure followed that of Brancio et al. [50].

Table 1 shows the results of an examination of considered interatomic potentials. We found that the hybrid potential shows considerable promise for modelling the structural changes under complex stress. Interestingly, the obtained results are equal to the weighted sums of the values calculated with the T2 and SW potentials. A slight deviation from the above rule is recorded for \( c_{44} \) which is likely related to differences in the course of structure relaxation performed with different potentials. The hybrid potential predicts the shear modulus \( c_{44} = 24 \) GPa, i.e. greater than \( c_{44} = 10 \) GPa calculated for T2, showing its higher resistance to the shear stress. We expect this advantage of the hybrid potential over T2 one allows reliable simulations of the interplay between phase transformations and dislocations activity during nanoindentation of Si crystal.

| Si phase | Space group | Lattice parameters \( a, b, c \) (Å), \( \alpha, \beta, \gamma \) (°) | Bond angle \( \theta \) (°) | Interatomic distance \( r \) (Å) |
|----------|-------------|---------------------------------|----------------|----------------|
| Si-I     | \( Fd\bar{3}m \) | \( a = 5.431 \) (8a) | 110 | 2.352 |
| bct5     | \( I4/mmm \) | \( a = 3.312, c = 5.959 \) (4e) \( z = 0.194 \) | 85, 107, 147 | 2.264, 2.449 |
| Si-II    | \( I4_1amd \) | \( a = 4.690, c = 2.578 \) (4a) | 75, 95, 105 | 2.432, 2.578 |
| Si-III   | \( Ia\bar{3} \) | \( a = 6.636 \) (16c) \( x = 0.1004 \) | 99, 117 | 2.306, 2.391 |
| Si-XII   | \( \bar{R}3 \) | \( a = 5.609, \gamma = 110.07 \) (2c) \( v = 0.2921 \) | 93, 99, 103 | 2.476, 2.319, 2.325, 2.374 |

| (6f) (0.4580,-0.0369,0.2645) | 118, 137 | 3.65, 3.74, 3.90, 3.97 |
| 112 | 4.32, 4.67, 4.78, 4.98 |

The data were moved to Supplementary Materials for clarity of the article.

Our simulations have been performed with the Lammps software [48] for a block of silicon crystal \((30.7 \times 30.7 \times 27.2 \text{ nm}^3, 1328142 \text{ atoms})\) indented with a rigid, spherical diamond tip \((R = 16.3 \text{ nm})\) in the \((001)\) plane. The coordination axes \((X,Y,Z)\) were aligned along the \([110], [1\bar{1}0] \) and \([001]\) Si crystal directions, respectively. Furthermore, the standard velocity-Verlet time integration scheme, with a time-step of 2 fs, was used through the simulations, while the Nose-Hoover thermostat was employed to control of the system. Prior to running nanoindentation simulations, the system was relaxed to a thermal equilibrium at the target temperature 300 K. Interactions between the diamond indenter tip and silicon crystal were modelled with the repulsive term of the Buckingham potential (the cut-off radius of 4 Å). MD-simulated nanoindentation of the Si crystal was accomplished by a sequence of rigid tip displacements with an increment of 0.5 Å every 15 ps, which in turn secured a quasi-static crystal deformation.

The deformed structure generated in the deformed Si crystal was examined in detail using tools (modifiers) incorporated into the OVITO software [51]. In order to obtain a clear presentation of the structural changes in the Si crystal caused by nanoindentation, atoms belonging to the diamond structure have been disregarded. The applied procedure (Identify diamond structure modifier) leaves only atoms whose arrangement corresponds to the non-diamond (high-pressure) phases of silicon. Moreover, the atoms have been attributed by the values of the shear strain (Atomic strain modifier). The identification of dislocations and their Burgers vectors was accomplished using a dislocation extraction algorithm (DXA modifier) [51, 52].

We have sought to verify our findings based on visualization of structural changes in nanoindentated silicon and by employing the bond-angle distribution function (BADF) and radial distribution function (RDF) to identify high-pressure silicon phases. The BADF was calculated by counting the bond angles in spheres with a radius 3 Å centred on each of Si atom. The range of bonding angles,
0 − 180°, was split into 200 section. Then the number of bond angles $N_i (i = 1, ..., 200)$ belonging to the specific $i$-th interval was calculated. As the groups of particles selected for structural analysis did not contain an equal number of atoms, we used the normalized distribution $N_i/N$, where $N$ stands for the number of atoms in the analysed group. A similar procedure was used in the case of the RDF, with interatomic distances determined within the spherical volume with radius of 5 Å.

3. Results and discussion

3.1. High-pressure silicon phases

At the beginning, we would like to supply more details on the transformations among the Si-I, bct5, Si-II, Si-III and Si-XII phases [53, 54]. Under normal conditions silicon has a diamond-cubic structure (Si-I) with the lattice parameter $a = 5.431$ Å. Diamond anvil cell (DAC) experiments show that when the pressure reaches about 10 GPa, the Si-I structure transforms to the metallic Si-II phase. When the pressure decreases, the Si-II structure does not return into initial Si-I, but instead, at 8.2 GPa, it transforms to rhombohedral Si-XII (r8) [55]. This metastable phase of silicon can be considered a distorted Si-III (bc8) one. Further decrease of the pressure removes the distortion gradually, and at the pressure of about 3 GPa, the system is the Si-XII/Si-III mixture. At the normal pressure, the system contains mainly the Si-III phase supplemented by a minor Si-XII component. Although the pressure-induced phase transition of Si-I→Si-II is not reversible, the reversibility of Si-XII→Si-III was confirmed [55]. The crystallographic parameters of Si-I, bct5, Si-II, Si-III, and Si-XII structures are presented in Table 2.

In order to describe the course of phase transformations induced by nanoindentation, it is necessary to consider one more high-pressure silicon phase, namely the theoretically discovered bct5 [56]. To the best of the authors' knowledge, no reports in the scientific literature would uniquely identify it under hydrostatic pressure condition. Instead, the nanoindentation-induced transformations to Si-II and bct5 phases were noticed as results MD simulations with Tersoff-type potentials [41–43, 57, 58]. A critical discussion of the Si-I→bct5 transformation based on a combination of indentation and Raman spectroscopy measurements was carried out in Gerbig et al. [7]. The initial conclusion that the bct5 phase appeared during the indentation was then modified by the finding [8] that it was instead dc2, i.e. a highly strained Si-I phase. The unloading of the indenter transforms the Si-II phase not directly into the Si-I one. Instead, the mixture of the Si-III/Si-XII [8, 9] and α-Si (amorphous) phases appear in a vicinity of the residual impression [16].

3.2. Nanoindentation of Si crystal

Nanoindentation induced deformation of the Si crystal, according to the hybrid potential prediction, begins with the emergence of a non-diamond (nd) phase at the indentation depth $h = 18$ Å and the contact pressure $p_c = 7.7$ GPa (Fig. 1a, snapshot 1). The nucleation of the nd structure occurs at the zone of increased shear strain, which, according to the Hertz theory of elastic contact, is located in some distance from the contact surface. As the indentation process unfolds, the detected non-diamond phase grows, reaching a stage when it undergoes the transition to the Si-II one (Fig. 1a, snapshot 2). The resulting Si-II volume ($h = 26$ Å, $p_c = 9.2$ GPa) expands further, forming a specific, compact grain of considerable volume adjacent to the contact area. Next, as straining increases, part of the material with the initial Si-I structure is transformed into another crystalline structure, as seen later, similar to Si-XII (Fig. 1, snapshot 3 and 4). The process takes place in four separated zones ($h = 36$ Å, $p_c = 10.7$ GPa), directly beneath and outside of the formed Si-II volume.

The BADF and RDF (Fig. 1b) distributions confirm the sequence of phase transformations that we have presented. The nd phase is characterized by the BADF peaks at about 110°, 125°, while the Si-II phase shows the peaks located at around 110°, 145°. The existence of the high-angle peak distinguishes the nd and Si-II phases from the initial Si-I which is characterized by the only one peak at exactly 109.47°. The BADF peak at about 125° recorded for the nd structure cannot be assigned to both bct5 and Si-II phase (see Table 2) as the latter exhibit peaks at 147° and 149°, respectively. Thus it indicates an existence of some precursor structure that precedes the Si-II formation. According to work by Gerbig et al. [8] one can recognize it as highly strained Si-I phase, i.e. dc-2. The RDFs show the peaks about that are not expected for Si-I phase, while they describes high-pressure nd and Si-II structures (compare with data in Table 2). A characteristic feature of the RDFs obtained for the Si-II phase is a presence of the peak at position about 3.1 Å which is close to the theoretically predicted locations at 3.04 Å. This peak increases gradually as the transition progresses to the Si-II phase. One can also observe that the BADFs collected during development of the Si-II phase are stable with respect to the peaks positions. Simultaneously, the RDFs exhibit small changes in the peaks locations, preserving their overall shape.

In order to provide crystallographic details of the phases predicted by the hybrid potential, we have visualized the atomic arrangements of the nd and Si-II structures. The unit cell of the nd phase (Fig. 1c) can be considered as similar to the unit cell of the bct5 phase. However, it can be also represented by a highly-strained Si-I tetragonal unit cell with $c/a$ ratio approaching the value slightly greater than 1 (1.08 for the cell in Fig. 1c), instead of $c/a = \sqrt{2}$ characteristic for cubic-diamond Si-I phase. This ambiguity in the determination of the nd structure likely reflects the mentioned earlier problem related to the correct description of nanoindentation-induced Si-I→Si-II transformation [7, 8]. Namely, is the formation of the Si-II phase accompanied/preceded by emergence of bct5 or dc2 phase? Interestingly, simulations with the hybrid po-
potential convinces that the \( nd \) structure exists as an intermediate state on the path from the Si-I to Si-II phase. Finally, inspection of the Si-II unit cell (Fig. 1d) reveals that its tetragonal parameter achieves the lowest value of \( c/a = 0.66 \) in the volume of large atomic shear strain, marked by white circle in Fig. 1a (snapshot 4). The lowest \( c/a \) parameter modelled by the hybrid potential is observed in the region of highest atomic shear strain and is slightly higher than experimentally expected value: \( c/a = 0.55 \) [53]. The Si-II structure in the proximity of the contact surface (low atomic shear strain) displays a value of \( c/a \) ratio of about 0.88.

After the Si-I \( \rightarrow nd \rightarrow Si-II \) transformation another phase transition is predicted by the hybrid potential. Namely, a Si-XII' structure appears instead of the Si-I, \( nd \) and Si-II phases. The hybrid potential convinces that the Si-XII' structure presented in Fig. 2a show that we are dealing with an arrangement of atoms that differ from those characteristic for the Si-I, \( nd \) and Si-II phases. The meaning of the symbol Si-XII' will soon become understandable.

In order to provide details of the Si-XII’ phase, we examined the bond angle and radial (Fig. 2b) distribution functions. The BADF peaks are located at 93°, 110° and 132°, and those for the RDF around 2.33, 3.39, 3.86, 4.28 and 4.84 Å. Comparing it with the data presented in Table 2 (mapped by brown vertical lines in Fig. 2b) one can convince that we obtained the phase with structural characteristics close to Si-XII rather than the Si-III phase. Indeed, the highest bond angle in Si-III structure, 117° has the value significantly lower that the 137° bond angle expected for Si-XII phase.

Fig. 2c and Fig. 2d show a local atomic arrangement of both the Si-XII' and Si-XII phases, respectively. The atoms highlighted by white circle lie closer to the viewer while the atoms without the circle lie further away from the viewer. The atoms labelled 1 and 2 are in the middle. The interatomic distances and bond angles calculated for both structures are presented in tables attached to Fig. 2. One can see that the main difference is related to the arrangement of atoms labelled 1, 6, 7, and 8. In the case of Si-XII' phase there is some symmetry among the bond angles which is not the property of Si-XII phase: \( \theta_{21} \approx \theta_{12} \approx 4°, \theta_{212} \approx \theta_{12} = 8°, \text{ and } \theta_{212} \approx \theta_{12} \approx 2\text{°}. \) The highest bond angle about 137° occurs twice \( (\theta_{212}, \theta_{212}), \text{ in contrast to the atomic arrangement of Si-XII phase for which the bond angle 137 exists only between atoms labelled 1 and 2). Roughly, it is possible to imagine that to obtain Si-XII atomic arrangement with the only one bond angle of 137°,
the atoms 6', 7', and 8' should be appropriately rotated around the axis passing through the atom 1' and lying in the plane of the figure and perpendicular to the segment 1'2'. The yellow arrows in Fig. 2c indicate approximate positions of atoms after the rotation.

The attractive property of the hybrid potential lies in the prospect of being able to model both phase transformations and dislocation processes in nanoindented silicon simultaneously. Figure 3 presents the development of the dislocation structure registered for \( h = 43 \) and \( 45 \) Å, together with high-pressure phases (Si-II and Si-XII') that exist at this stage of nanoindentation. The DXA analysis enables us to identify the dislocation lines in the \( \{111\} \) planes, and to determine their Burgers vectors as \( 1/2<110> \). It is also worth noting that the expansion of dislocations assume the correct orientation, namely, downwards into the crystal volume (Fig. 3), which agrees with experimental observation [16]. In this way, modelled by the hybrid potential, the nanoindentation induced plastic deformation of silicon begins with phase transition, and then, when the stress level reaches an appropriate level, dislocation nucleation occurs.

Additionally, we have simulated the unloading path of the nanoindentation (Fig. 4). Beginning with the crystal state shown in Snapshot 4 in Fig. 1a, we moved the indenter up with 0.5 Å increment. The crystalline high-pressure silicon phases gradually disappeared. After complete unloading, the only dislocation net and the volume of the amorphous Si phase remained near the deformed surface (Fig. 5). The depth of the residual impression is approximately 7 Å, while the amorphous Si occupies an area of an approximate V-shaped cross-section between 23 Å and 97 Å from the crystal surface.

3.3. Final remarks

Wong et al. [10–12] showed that under certain experimental conditions, nanoindentation can generate a compact volume occupied by a mixture of the Si-III (bc8) and Si-XII (r8) phases which is adjacent to the contact surface. The Si-III/Si-XII phase volume was observed after nanoindentation, so it can be expected that just before the unloading, the Si-II phase filled a comparable volume in contact with the crystal surface. Interestingly, modelled by our hybrid potential compact grain of Si-II phase is in contact with the crystal surface (Fig. 1a, Snapshot 3 and 4). It is in stark contrast to the result obtained with
of Si crystal were performed employing Raman spectroscopy. Thus, Gerbig et al. [8] have been able to provide experimental proof that the Si-I→Si-II transition is accompanied by the formation of the dc-2 structure, which is referred to as a highly strained Si-I phase. Likely, the dc-2 lattice has earlier been mistaken for bct5 [7] as the interpretation of the spectroscopic data based on MD-simulations with a non-screened Tersoff-type potential [57, 58]. Interestingly, the ambiguity contained in our description of the unit cell of the nd phase (Fig. 1 c) opens the question of which phase precedes the formation of the Si-II phase. It needs emphasizing however that the bct5 phase does not show up either in the Raman spectroscopy studies or in simulations performed with the hybrid potential (Fig. 2), featuring only in simulations performed with the Tersoff-type potentials, including T3s (Figs. S1-S3). As the bct5 phase was not observed experimentally during nanoindentation of Si crystal, the results obtained with our hybrid potential seems to reflect reality more precisely. Finally, we would like to point on the feature of the hybrid potential, which neither T2 nor SW do not exhibit. It is emergence of nd phase before formation of the Si-II one. Surprisingly, the existence of the nd phase also predicts the T3s potential (Fig. S3) founded on a serious physical arguments [36].

Another point worth noting is that simulations with the hybrid potential enabled the detection of the high-pressure Si-XII’ structure in the late stage of the loading of the indenter (Fig. 1a, Snapshot 3 and 4). Remarkably, we have been able to come across only one recent publication to locate the emergence of the Si-XII phase in the loading stage of nanoindentation, namely by Gerbig et al. [9]. It concerns nanoindentations performed with the Berkovich indenter accompanied by the Raman spectroscopy characterization of microstructural changes during indentation. The Raman traces of a mixture composed of Si-III and Si-XII phases was detected in the centre of a deformation zone. This surprising result complete common interpretation of nanoindentation-induced deformation of Si crystal, which pointed out that formation of Si-III/Si-XII phases is an effect of stress relaxation during unloading of the indenter. Although modelled by the Si-XII’ hybrid potential structure only resembles the ideal Si-XII phase, the reader can again conclude that the proposed hybridisation of the T2 and SW potentials gives results describing a fuller range of structural phenomena occurring during silicon nanoindentation.

Our main point of reference is the Tersoff-type screened potential developed by Pastewka et al. [36]. This T3s potential, which to date represents the most advanced approach to the complex deformation of Si crystal induced by a nanoindentation, takes into account both dislocation...
activity and phase transitions [41] [43]. Although the T3s- and hybrid-driven simulations reveal dislocation activity and phase transformations that contribute to the overall indentation deformation, there are some crucial differences between the two. One of them is that an uneven, i.e., along the slip planes, distribution of the Si-II phase which has already been discussed. Another example is the contact pressure value at the onset of Si-I→nd and nd→Si-II transformations. In the case of the hybrid potential, we obtained the values of 7.7 and 9.2 GPa, respectively, which are significantly lower and closer to the reality that 15.9 and 17.8 GPa obtained with the use of the T3s potential (refer to Fig. 4). It is also worth noting that in the scenario obtained with the hybrid potential, slip leads to the generation of large, extended linear defects on the {111} planes that develop outwardly of the Si volume occupied by high pressure phases (Fig. 3 and Fig. S4). The situation looks different in the case of the T3s potential where slip, while also occurring along the {111} planes, generates limited dislocations in the direction parallel to the (001) surface of the Si crystal (Fig. S5).

4. Conclusions

In summary, we have developed a hybrid potential with increased transferability, which enables modelling of the phenomena that occur in nanoindented Si crystals in good agreement with earlier experiments. MD simulations with the hybrid potential provide a realistic contact stress at the onset of a plastic deformation of silicon. Moreover, new potential makes it possible to reflect the subsequent stages of Si nanodeformation, such as a transformation to the Si-II phase, the formation of an Si-XII-like structure as deformation proceeds and, finally, the dislocation generation.

Noticeably, refreshed by us, the potential hybridization method may increase the transferability of the existing potentials. In terms of efficiency, the method is remarkably fast and sparing of computational resources by comparison with the machine-learning potentials. Furthermore, hybridisation has been shown to produce an interaction model for an extended range of physical phenomena, establishing an alternative for the most prominent potentials now available. Last but not least, the hybridisation method’s ready availability will satisfy the demand for a quick way to construct interatomic potentials by opening up the vast library of existing ones to new applications.

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Silicon nanoindentation modeled by hybrid potential

by

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1. Supplementary figures (Figs. S1-S5)

**Fig. S1** MD-simulations with the T3s potential. (a) Selected indentation stages 1-4, \((h = 21.5, 23.5, 25.0 \text{ and } 30.0 \, \text{Å})\) showing evolution of high-pressure bct5 and Si-II phases during nanoindentation. (b) The bct5 and Si-II phases from snapshot 4 shown here in focus as unit cells.
Fig. S2 The distribution of the high-pressure Si phases modelled with the $T_{3s}$ potential. (a) Location of cross-sections (5 Å thick lamellae) of the high-pressure Si phases formed under a rigid spherical indenter ($h = 39$ Å, $p_c = 20.3$ GPa). Snapshots 1-7 ($y = -60, -40, -20, 0, +20, +40$, and $+60$) demonstrate that high-pressure phases do not represent a compact volume adjacent to the contact surface, in contrast to the prediction with the hybrid potential. The effects associated with shear-bands are marked in yellow arrows, while the formation of bct5 and Si-II structure in blue and red, respectively.
**Fig. S3** Modelling with the T3s potential shows the nd structure. (a) The nd phase in 20 Å thin lamellae of Si crystal (vertical section along indenter symmetry axis) is positioned approx. 30 Å below the contact area. Atom colour specifies shear strain level. (b) Si structure rotated to demonstrate location and atom arrangement of nd area marked by open circle. Extracted unit cell of the nd phase shows deviation from bct5 structure. The nd unit cell can be represented by the highly compressed tetragonal Si-I phase. (c) BADF and RDF functions at the $h = 20$ Å indentation depth, reveal structural differences between nd and Si-I phases.
**Fig. S4** Modelling with the **hybrid** potential shows the visualization of the slip planes on which the dislocations develop during nanoindentation (refer to Fig. 3 in the main text). The most interestingly the dislocations does not develop parallel (Fig. S4) to the indented surface, but downwards the crystal – as observed in reality, contrary to the scenario imposed by the simulations with $T3s$ potential.

**Fig. S5** MD-simulations with $T3s$ potential showing the evolution of dislocation structure in the nanoindented Si crystal. The sequence of snapshots (1-4) taken for respective indentation depths of $h = 25$, $30$, $35$ and $39$ Å provide the DXA based visualization of dislocation structure and its development. The defects (the Burgers vector defined in the figure) are generated in the $\{111\}$ planes, outside of the regions occupied by high-pressure Si phases.
2. Supplementary text: The hybrid HPI potential and Lammps

In order to implement the hybrid potential in the Lammps simulation package, the parameters of the T2 and SW component potentials were modified according to equation

\[ E_H = w_{T2} E_{T2} + w_{SW} E_{SW} \]

where

\[ w_{T2} = 0.71875, w_{SW} = 0.28125 \]

The pertinent Si potential files are as follows:

a) The case of SW potential

```
# file: Si.sw.28125
# element 1, element 2, element 3, epsilon, sigma, a, lambda, gamma, costheta0, A, B, p, q, tol
# Stillinger and Weber, Phys. Rev. B, v. 31, p. 5262, (1985)
# lambda: 5.90625 = 21.0 \times 0.28125
# A: 1.982687703 = 7.049556277 \times 0.28125
Si Si Si 2.1683 2.0951 1.80 5.90625 1.20 -0.333333333333 1.982687703 0.6022245584 4.0 0.0 0.0
```

b) The case of T2 potential

```
# file: Si.tersoff.71875
# element 1, element 2, element 3, m, gamma, lambda3, c, d, costheta0, n, beta, lambda2, B, R, D, lambda1, A
# Tersoff, Phys Rev B, 37, 6991 (1988)
# A: 2346.503125 = 3264.7 \times 0.71875
# B: 68.54934375 = 95.373 \times 0.71875
Si Si Si 3.0 1.0 1.3258 4.8381 2.0417 0.0000 22.956 0.33675 1.3258 68.54934375 3.0 0.2 3.2394 2346.503125
```

Moreover, nanoindentation deformation was simulated using scripts containing the Lammps commands which define the Si-Si and Si-C interactions, as follows:

```
... 
mass 1 28.085
mass 2 12.011
pair_style hybrid/overlay tersoffsw buck 4.0
pair_coeff * * tersoff Si.tersoff.71875 Si NULL
pair_coeff * * sw Si.sw.28125 Si NULL
pair_coeff 1 2 buck 100.0 0.6 0.0
pair_coeff 2 2 none
... 
```