

Nondislocation Origin of GaAs Nanoindentation Pop-In Event

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The present Letter demonstrates a pop-in event that is caused by a nanoindentation-induced phase transformation in GaAs, and not accompanied by any dislocation nucleation. Our computer simulations reveal the appearance of the new phase, documented by the structural correlation functions and visualization of the atomic positions. This challenges the orthodox view that the initial pop-in event reflects nucleation of dislocations or their movement, and has a bearing on materials where dislocation activity is not present.

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Recent advances in atomistic scale plasticity are due to atomistic simulations of nanodeformation of crystals on the one hand, and to nanoscale indentation experiments—in which a tiny volume of the solid deformed under the tip is probed—on the other. One of the most exciting aspects of nanoindentation of materials concerns the so called “pop-in events” [1,2], where the indenter suddenly enters deeper into the material without any additional force being applied. Recent findings suggest that the origin of the initial pop-ins in crystals could be explained in terms of homogeneous [3–5], or heterogeneous [6] dislocation nucleation under the penetrating tip. This has been repeatedly demonstrated for metals [1–3] and more recently for SiC [4]. Dislocation nucleation also seems to account for the newly discovered reversible plasticity in metals [7], scale-free intermittent flow in crystal plasticity [8], and agrees with the observations of defect nucleation in colloidal crystals [9]. A dislocation-based explanation has also been offered for pop-in events observed in GaAs [10,11].

In the current Letter we carry out computer simulations which show that, at least in GaAs crystal, a pop-in event can result neither from dislocation nucleation nor defect-activity, reflecting instead a crystalline-to-crystalline phase transition. The reversible nature of this transformation explains why it has not so far been detected in nanoindented GaAs.

We have used a tailored version of the molecular dynamics (MD) code PARCAS by Nordlund *et al.* [12], capable of simulating both dislocation activity as well as phase transitions in a near-surface region [12,13]. The computer experiments used a simulation cell composed of 700 316 atoms that formed a perfect cuboidal crystal of GaAs (size of $316 \times 316 \times 158 \text{ \AA}$) with its typical zinc-blende structure ($a_{\text{GaAs}} = 5.635 \text{ \AA}$) and four bottom atomic layers immobilized, i.e., rigorously kept in a fixed location. To perform a quasistatic simulation of the nanoindentation process into the (001) plane of GaAs, the crystal was “set in contact” with a diamond ($a_{\text{diamond}} = 3.567 \text{ \AA}$) cubic-indenter (size of $28 \times 28 \times 28 \text{ \AA}$) [14], similarly

to the cubic-tip indentation into SiC-crystal modeled by Szlufarska *et al.* [3] The C-Ga and C-As interactions were realized by the universal Ziegler-Biersack-Littmark purely repulsive potential [15]. The atomic interactions within GaAs were modeled using a three-body Tersoff-type potential [16] that had been constructed to describe both first and second-order elastic constants of this compound as well as several other crystalline structures of GaAs in addition to the zinc-blende one.

The mechanical response of the MD-simulated tip-GaAs system was analyzed in terms of total potential energy $E(h)$, presented in Fig. 1(a), which provides depth resolution of the force absolute value $F(h) = dE/dh$ experienced by the tip [Fig. 1(b)]. Interestingly, the obtained $E(h)$ function is parabolic for indentation depths h not exceeding $h_{\text{pop}} = 3.12 \text{ \AA}$, while appearing linear beyond

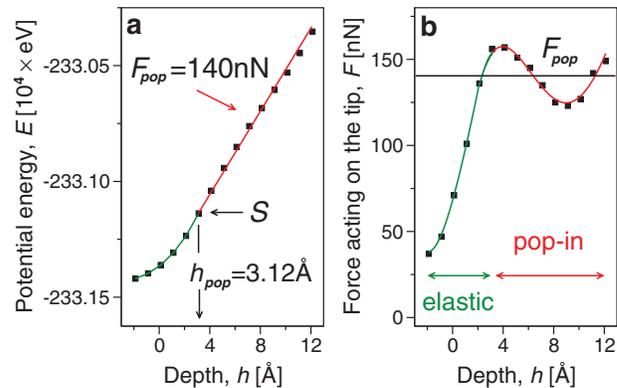


FIG. 1 (color). The variation in potential energy E of a GaAs crystal deformed in the course of consecutive depth increments Δh of penetration into the (001) plane (a), and the nanoindentation load-depth $F-h$ data (b) obtained by the derivation of the $E(h)$ relationship [$F(h) = dE/dh$]. The singularity S at the depth $h_{\text{pop}} = 3.12 \text{ \AA}$ marks transition from a parabolic (green) to linear (red) $E(h)$ relationship (a) and denotes the starting point of GaAs pop-in (b) that occurs under the force mean value $F_{\text{pop}} = 140 \text{ nN}$.

the singularity S [Fig. 1(a)]. The point S marks the moment after which the deformation proceeds under a roughly constant load $F_{\text{pop}} = 140$ nN. This corresponds to the sudden depth excursion reflected by the $F-h$ curve [Fig. 1(b)], i.e., a pop-in behavior similar to that revealed by nanoindentation experiments for GaAs crystals. This has been attributed either to dislocation generation under the tip [10], or their collective movement within slip bands in the deformed zone [11]. The force drop observed after an initial yielding [Fig. 1(b)] is characteristic of depth-controlled nanoindentation tests [3], providing further proof that our simulations were consistent with experimental behavior.

To determine whether the pop-in registered by us reflects dislocation nucleation, we used the method by Zimmerman *et al.* [17] (see Ref. [14]). Despite our efforts, we did not detect any dislocation under the acting tip, which resembles investigations of silicon by Sanz-Navarro *et al.* [18], who also failed to find dislocations in the indented region. This made us suspect that a phenomenon other than dislocation generation was at play in GaAs crystals, and that the frequently reported dislocation activity under the acting tip [10,11,19] based on microscopic observations was associated with later stages (post pop-in) of indentation.

To arrive at the origin of the pop-in event, the structural changes induced in GaAs during nanoindentation were examined using radial (RDF) and bond-angle (BADF) distribution functions determined for Ga-As pairs and Ga-As-Ga as well as As-Ga-As angles, respectively. Nanoindentation in the (001) plane of GaAs results in a widening and simultaneous decrease of the main peak height both for the RDF and BADF functions illustrated in Figs. 2(a) and 2(b). This effect is accompanied by the appearance of new peaks in the RDF-function for the interatomic distance d of approximately 3.3 Å [Fig. 2(a)], and more importantly, in the BADF spectrum at the locations θ equal to 70° and 90° [Fig. 2(b)], which are inconsistent with the GaAs zinc-blende structure that we started to deform. Variations in the distribution functions reflect the changes in the arrangement and number of the nearest neighbors [RDF, Fig. 2(a)] and the emergence of a configuration with 90° bonding angles [BADF, Fig. 2(b)] characteristic of the rocksalt structure of GaAs [20,21].

The deformed structure, when restricted to a smaller cuboidal volume (size of $28 \times 28 \times 17$ Å) of GaAs crystal (here called U domain), was found to possess 521 sixfold coordinated atoms with bond lengths that did not exceed 3.6 Å. The RDF function revealed two sharp, well-developed peaks at interatomic distances of 2.5 and 3.3 Å [Fig. 2(c)], while the BADF function provided clear evidence that a new GaAs phase prevailed in the U domain [Fig. 2(d)]. Indeed, the majority of bond-angle values concentrate close to 90°, in contrast to the GaAs zinc-blende structure with a preferred bond angle of 110° [Fig. 2(d)]. This demonstrates that GaAs' is the dominant phase in a large part of the specific U region.

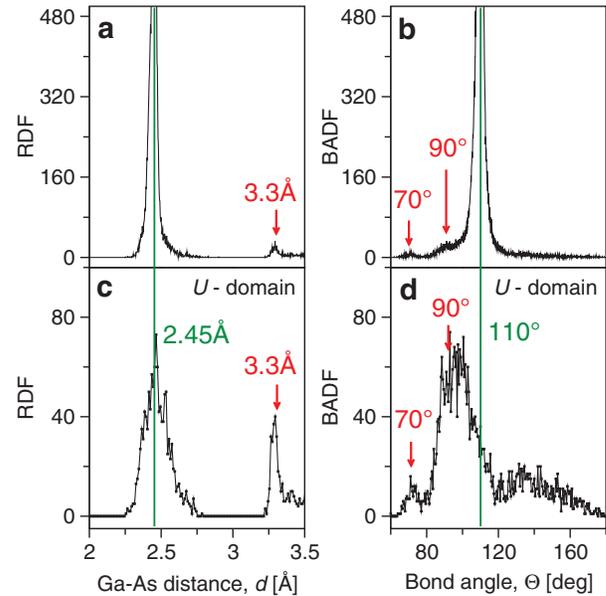


FIG. 2 (color). The RDF (a),(c) and BADF (b),(d) functions determined for the entire deformed area of the GaAs crystal (the indentation depth $h_{\text{max}} = 12.12$ Å) (a),(b) as well as a restricted volume (U domain) located directly under the indenter (c),(d). The former (a),(c) define the predominant Ga-As distance, while the latter (b),(d) the bonding angle. Green lines mark the locations of the peaks for an undistorted GaAs zinc-blende structure, while the BADF-peak, in the position of 90°, detected in a deformed solid, is typical a GaAs rocksalt lattice. The marked peak observed for an interatomic distance of 3.3 Å (c) and, more importantly, the preferred concentration of bond angles around 90° (d) shows that, in the highly stressed U domain, one is dealing with a new phase of GaAs.

In the absence of any dislocation-nucleation mechanisms in our material, it is perfectly reasonable to assume that the pop-in phenomenon in Fig. 1(b) is associated with a nanoindentation-induced phase transformation from an initial zinc-blende structure to a new GaAs' phase. There have been indications that not all of the pop-in events are necessarily related to dislocations. In a study of sapphire by Nowak *et al.* [22–25] it was found that it was a twinning type transformation, rather than a nucleation of dislocation-loops in Al_2O_3 , which was responsible for the pop-in effect. Furthermore, Li *et al.* [26] also considered the possibility of structure transition in an indented GaAs based on some earlier results of pressure-cell experiments [27], but they failed to detect a new phase by TEM observations.

The nanoindentation-induced transformation of GaAs to GaAs' phase, revealed by an MD simulation, resembles the transition from GaAs zinc-blende to the rocksalt structure observed during anvil experiments under a hydrostatic pressure of 16–23 GPa [20,27]. Furthermore, theoretical calculations [21] showed that the pressure-induced GaAs phase represents an orthorhombic, distorted rocksalt structure with a preferred atom coordination number of six and a

characteristic bond angle equal to 90° , precisely the figures that we obtained in our simulations (see Fig. 2).

Taken together, the consistent results of our analysis of the atomic distances and angular distribution functions, the lack of dislocations in the deformed volume, and finally, the level of pressure (18 GPa) generated under the acting indenter (details in Ref. [14]), all lead to the conclusion that we are witnessing an unreported nanoindentation-induced phase transformation from a GaAs zinc-blende to a rocksalt structure. Indeed, it is this transformation, which itself turns out to be a hitherto unknown cause of the discussed pop-in event.

The final and decisive confirmation of the proposed state of affairs comes from direct visualization of the GaAs structure that undergoes deformation in a computer-simulated nanoindentation experiment. The image of the atomistic structure of GaAs under the tip that penetrated to the depth $h_{\max} = 12.12 \text{ \AA}$ into the (001) plane was obtained from MD simulations. Figure 3(a) illustrates the atom arrangement in a nanoindented GaAs crystal viewed along the [111] direction, thus exposing the contrast between (i) the GaAs' structure of the highly stressed

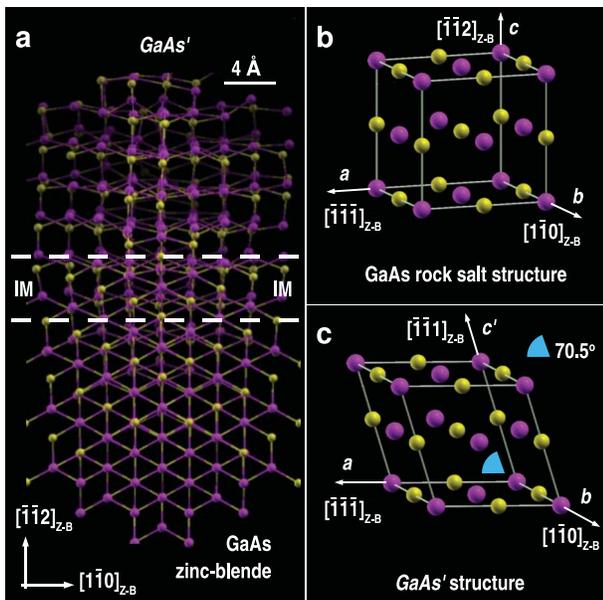


FIG. 3 (color). Direct visualization of: the atomic positions determined for a nanoindented ($h_{\max} = 12.12 \text{ \AA}$) GaAs crystal viewed along the [111] direction (a), the orientation of the GaAs rocksalt unit cell with respect to the zinc-blende lattice (b), and the GaAs rocksaltlike structure generated under the acting indenter (c). The GaAs' ordering resembles that of a GaAs rocksalt structure (b). The $[\bar{1}\bar{1}\bar{1}]$, $[1\bar{1}0]$, and $[\bar{1}\bar{1}2]$ directions of the zinc-blende configuration (b) define the principal vectors \vec{a} , \vec{b} , and \vec{c} of a rocksalt unit cell, respectively. The \vec{c}' vector coincides with the $[\bar{1}\bar{1}\bar{1}]$ direction for a rocksaltlike arrangement (c) and forms the angle of 70.5° with the direction, in accord with the BADF analysis [Figs. 2(b) and 2(d)]. IM defines an intermediate region with a mixed arrangement of Ga (magenta) and As (yellow) atoms.

U domain, (ii) the atom architecture of the intermediate zone (IM), and (iii) the zinc-blende arrangement preserved in untransformed GaAs.

Clearly, the well-developed crystallographic planes of the new GaAs' phase must have been formed in a highly stressed region of the investigated crystal. The GaAs' phase is characterized by the arrangements of Ga and As atoms located at a distance of 2.5 \AA from each other along the $[1\bar{1}0]$ and $[\bar{1}\bar{1}1]$ directions, while the interatomic spacing in the $[111]$ direction equals alternatively 2.5 and 3.3 \AA [Fig. 3(c)], as already detected by our RDF-analysis [Fig. 2(a)].

All of the properties of the GaAs' phase described above are consistent with those of a distorted rocksalt one (henceforth called rocksaltlike structure) [28]. Having established that a new crystalline phase actually does form, an explanation of the linearity of the total potential energy follows naturally [Fig. 1(a)]. It is the consequence of the energy consumption required for the transformation of a GaAs structure to a rocksaltlike one; once the critical pressure for the transition is reached and the initial nucleus of a new phase is formed, the total potential energy can rise with a linear increase. This is confirmed by the fact that the number of bond angles within the range of 80° to 95° (characteristic of a rocksaltlike structure) increases with penetration depth exactly in the same manner as does the potential energy [compare Figs. 1(a) and 4]. The force-drop and its successive rise within the pop-in [Fig. 1(b)] is due to a decrease of stress during phase transformation and the subsequent straining of the entire crystal, respectively.

The pop-in event has been observed in GaAs during nanoindentation experiments on many occasions [10,11,19]. The effect has been attributed either to dislocation rosettes [10,19] or slip band formations [11], which contradicts the results of our research. Moreover, several

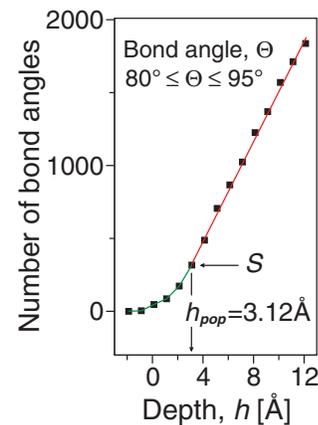


FIG. 4 (color). Depth dependence of a number of bond angles, between 80° and 95° , characteristic of a GaAs rocksalt structure. The obtained relationship reflects the depth-resolution of the total potential energy $E(h)$ [Fig. 1(a)], supporting our concept of GaAs pop-in behavior as having its origin in phase transformation.

declarations based on post-indentation structural investigations deny any trace of a new GaAs phase. Li *et al.* [26], for example, claimed that the tiny remnant amorphization on an indented GaAs surface is all that remains after indentation process.

To solve the apparent dilemma between our calculated results and nanoindentation experiments, we performed MD simulation of the entire unloading path in GaAs, which made us discover that the GaAs rocksaltlike structure undergoes almost complete reverse transformation to the original zinc-blende configuration, while a tiny part of the new phase turns amorphous during the recovery. This closely resembles the findings by Li *et al.* [26], as well as the anvil-cell experiments by Benson *et al.* [27], whose pressure release experiments involved a similar GaAs transition accompanied by limited amorphization. The atomistic aspect of pressure-induced phase transformations was also studied by Rino *et al.* [29], whose results agree with our output. Thus, given the reversible character of the transition, it becomes clear why the experiments were unable to discover a transformed GaAs phase after indentation. The advocates of dislocation-related pop-ins, e.g., Leipner *et al.* [10] or Bradby *et al.* [11], were examining GaAs samples loaded well above the pop-in force, which obviously activated dislocation mechanisms during the later stages of deformation (after pop-in). One should however keep in mind that real crystals frequently contain defects, which may significantly affect the incipient plasticity.

In sum, the present study shows that the origin of the pop-in phenomenon, already well documented for GaAs crystals, is a phase transformation from a zinc-blende structure to a rocksaltlike one that occurs under the acting indenter. Apart from clarifying the deformation of GaAs during nanoindentation, it challenges the orthodox view that the initial pop-in event always reflects a nucleation of dislocations or their movement. What appears to be the case is that the pop-in effect may also be caused in materials where suitable phase transformation paths exist—by atomic rearrangement due to a phase transformation under the acting indenter.

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