Self-healing of fractured one dimensional brittle nanostructures

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Abstract

Recent experiments have shown that fractured GaAs nanowires can heal spontaneously inside a transmission electron microscope. Here we perform molecular dynamics simulations to investigate the atomic mechanism of this self-healing process. As the distance between two fractured surfaces becomes less than 1.0 nm, a strong surface attraction is generated by the electrostatic interaction, which results in Ga–As re-bonding at the fracture site and restoration of the nanowire. The results suggest that self-healing might be prevalent in ultrathin one-dimensional nanostructures under near vacuum conditions.

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Self-healing is a widely observed phenomenon in natural materials, particularly in biomaterials such as the healing of a small cut in skin and restoration of fractured bones. Mimicking biological systems, scientists have been inspired to design materials that have the ability to restore their mechanical properties and functions after damage [1–4]. Since self-healing behaviors have been observed in a wide range of nanostructured materials, e.g. ceramic nanocrystals, carbon nanotube and graphene, it has become an important emerging field of nanotechnology [5,6]. In synthetic materials, there is no circulatory system to mimic the biochemical components of self-healing in a living body, and thus, a more direct route to self-healing is re-bonding of atoms at the fracture site. However, this cannot happen in a macroscopic system where damaged surfaces are often so rough that even mechanical contact is impossible. At nanoscale, however, surface roughness would be limited by the characteristic dimension of the structure. With the distance between two fractured surfaces substantially reduced, atoms on one surface can react with their counterparts on the opposite side. It can thus be expected that self-healing might be prevalent in one dimensional nanostructured materials, such as GaAs nanowires (NWs), SiC NWs, ZnO and GaN NWs or nanobelts, and carbon nanotube, at least under near vacuum conditions. The healing efficiency of these NWs can hardly be evaluated by experiments since the lateral dimension of an individual NW is less than 12 nm [7]. Such a gap, however, could be at least partially filled with numerical simulations.

The present work is motivated by recent in-situ deformation experiments that demonstrated repeatable self-healing of fractured GaAs NWs inside a transmission electron microscope [7]. It was speculated that surface attraction, oriented-attachment, nanoscale dimension and atomistic diffusion are possible reasons to have induced the observed self-healing behavior, but the actual operative mechanism is still elusive. Here we report molecular dynamics simulations of the self-healing process between fractured sections of a GaAs NW. The results will show that self-healing between two fractured surfaces is an intrinsic property of one-dimensional brittle nanowires.

In our molecular dynamics simulations, we consider a zinc-blende structured GaAs NW with wire axis in the [111] direction and (110) type side facets, as illustrated in Fig. 1(a) [8,9]. The GaAs NW has a cross-sectional dimension of 5.5 nm and an aspect ratio of about 6:1. A potential consisting of two-body and three-body covalent interactions is adopted to define atomic interactions in the molecular dynamics calculations [10]. Here, it is worth noting that the charge transfer and charge-induced dipole interaction due to the large polarizability of negative ions have been included in the interatomic potential. Thus, this potential can be used to describe the (001) surface reconstruction of GaAs. However, such a kind of reconstruction has no influence on the self-healing of GaAs NWs because fracture occurs along the (111) surface. *Ab initio* simulations could possible enhance the accuracy of the results, but are impractical for the system sizes analyzed here.

To simulate uniaxial tensile loading, an increasing strain in the [111] direction is imposed in two steps: First, a modified isothermal-isobaric ensemble is used to stretch the GaAs NW at a strain rate of 0.001 ps^{-1} for 1 ps [11]; then the axial strain is held fixed while the NW is relaxed for 6 ps via a canonical ensemble to obtain its mechanical parameters [12]. In each loading step, the nominal strain is increased by ± 0.1% (corresponding to an elongation of about 0.33 nm). The effect of loading rate is examined by reducing the imposed strain rate by a factor of 10, with no significant discrepancy detected. The system temperature is maintained at 300 K. All samples are relaxed for 20 ps before stretching or attaching operation. The stress is calculated by a modified virial formula [13]. All the calculations were carried out by using the DL_POLY2.20 package [12]. More details on numerical simulations are discussed in Ref. [14].

We perform MD simulations to assess the mechanism of self-healing in GaAs NWs in vacuum in the following order: tensile loading of a NW to fracture → self-healing of the fractured NW → re-loading of the healed NW. Firstly, uniaxial tensile loading is applied on the selected NW until fracture. The two fractured sections are then attached along their axes. Finally, uniaxial tensile loading is re-applied while the mechanical properties of the restored NW are evaluated.

The uniaxial tensile loading imposed on a virgin GaAs NW leads to brittle fracture between two neighboring (111) planes, as shown in Figs. 1(b) to (d). The two fractured surfaces are terminated with Ga and As atoms, respectively, and their morphologies exhibit roughness with a thickness of about one atom.

As shown in Fig. 2, a typical self-healing process consists of three stages: attaching, contacting and healing. (1) As the distance between two fractured surfaces exceeds 1.0 nm, no interaction between them can be detected. (2) As the distance is reduced from 1.0 to 0.7 nm, substantial surface attraction emerges (see Fig. 2(a)). The attractive force per unit area is about 0.1 GPa, which enables a small amount of broken Ga–As bonds between two fractured surfaces to reconnect, as shown in Fig. 2(b). (3) With further reduction of distance, the surface attraction between two fractured surfaces reaches a maximum of 0.87 GPa, which is much stronger than that in the contacting stage. The two peaks of surface attraction in Fig. 2(a) correspond to two healing events: partial healing in rough regions (peak A) and full healing of the fractured NW (peak B). It is worth noting that, however, the fractured GaAs NW cannot completely restore its original structure, as shown by the scar remaining on the self-healed surface in Fig. 2(c).

The tensile test on the self-healed GaAs NW shows that the tensile strength can reach 7.19 GPa. In comparison with the original strength of 9.27 GPa for the virgin NW, it is seen that 77.6% of its tensile strength is restored (see Fig. 3). Moreover, the Young's modulus (138.0 GPa) of the self-healed GaAs NW is almost the same as that of the virginal one (138.7 GPa). Here, it is of interest to note that the second brittle failure at the end of re-loading happens at the same location. In subsequent simulations, we performed repeated cycles of fracture and healing. As shown in Fig. 4, the healing efficiency decreases from 77.6 to 36.0% in 15 cycles, with a reduction of 3.43% per cycle.

Our simulation results provide some useful insights into the self-healing behavior in GaAs NWs. When a GaAs NW is subjected to tensile loading, fracture occurs between two neighboring (111) planes. The fracture morphology can be strongly influenced by the choice of interatomic potentials [15]. In our simulations, the fractured (111) surfaces are consistent with the theoretical cleavage along close-packed atomic planes. The generated atomic scale roughness (one to two atom layers thick) on fractured surfaces is due to stochastic bond-breaking at neighboring (111) planes. The ultrathin lateral dimension of GaAs NWs provides relatively smooth fractured surfaces, which are mainly occupied by oppositely charged Ga and As atoms. As the distance between two fractured surfaces falls below 1.0 nm, surface attraction emerges as a result of the near-field electrostatic interaction. At a long distance, the Coulomb interaction between two fractured surfaces quickly declines due to the alternate arrangement of oppositely charged Ga and As ions. At a smaller distance, the attraction can be strong enough to pull those atoms located at opposite fractured surfaces together and induce Ga–As re-bonding. The original structure of a GaAs NW can be restored to a large fraction of its original strength through large scale re-bonding at the fractured site. The similar role of surface attraction has been also observed in a large number of nanostructures with strong ionic bonding, such as ZnO, CdSe and PdSe nanocrystals [16–20].

During the self-healing process, the oriented-attachment operation contributes to the efficiency of healing (i.e., the percentage of restored strength) because the two fractured sections are all [111] oriented with corresponding fractured surfaces along the (111) planes. Such an operation ensures that atoms and the Ga–As bonds can rebind without too much strain misfit. Similar mechanisms were reported in PdSe nanocrystals and Au NWs [18,21]. Due to the non-polar nature of gold atoms, other forces such as the van der Waals interaction are likely to play more important roles. We note that atomic mobility may have affected the healing process observed in experiments [7,21]. However, such processes cannot be appropriately modelled by molecular dynamics simulations.

Potential obstacles to healing of fractured GaAs NWs include impurities, local defects and roughness of fractured surfaces. Although the roughness on the fractured GaAs NW surfaces is only a few atom layers thick, it can prevent more atoms from entering the effective range of surface attraction. The roughness also causes mismatching of atoms during healing. Thus, the original structure of a virgin NW cannot be entirely restored. Local structural defects in the self-healed GaAs NW become the source of damage nucleation during re-loading. As a result, the self-healed GaAs NW shows a slightly lower Young's modulus and substantially lower tensile strength. The negative influence of surface roughness on self-healing was also recognized in the case of polymers [22].

Self-healing between two fractured sections may be an intrinsic property of a wide range of one-dimensional nanostructures such as carbon nanotube, SiC, ZnO and GaN NWs or nanobelts. Brittle failure of these nanostructures generates relatively smooth fractured surfaces, and re-bonding between two fractured surfaces can be achieved through surface attraction in the near-field region under oriented-attachment. As listed in Table I, the GaAs NW possesses both the highest surface attraction and healing efficiency [23]. No apparent attraction was detected in a healing process of carbon nanotubes because of the extremely short distance of covalent interaction between C–C bonds. Although GaAs and SiC NWs have the zinc-blende structure, the Ga–As bond is more ionic than Si–C [24]. Due to its long-range nature, ionic interaction can link atoms on fractured surfaces from a moderate distance. Covalent interaction in SiC, however, dominates in a short range. Due to the lack of oriented-attachment, mismatch may occur during Si–C re-bonding. As a result, the healing efficiency of GaAs NWs is more than that of SiC NWs. The low healing efficiency of ZnO and GaN NWs seems to be due to their polycrystalline nature, which results in more rough fracture surfaces [25]. In the case of carbon nanotube, plastic deformation may further reduce the healing efficiency. The corresponding operation is usually referred to cold-welding, where original lattice structures cannot be restored [21]. Thus, enhancing atomistic diffusion can be a better strategy to improve performance of those with lower healing efficiency [26].

In summary, molecular dynamics simulations have been carried out to investigate the self-healing mechanism of a fractured GaAs NW. The results show that the smooth fractured surfaces only with atomic scale roughness in a NW is a major factor that contributes to the self-healing of the fractured GaAs NW. Strong surface attraction due to electrostatic interaction is detected as the distance between two fractured surfaces falls below 1.0 nm. We conclude that self-healing in GaAs NWs is achieved from re-bonding between Ga and As atoms on two fractured surfaces. The present study suggests that self-healing may be an intrinsic property of ultrathin one-dimensional brittle nanostructures, and that more novel nanostructured materials can be designed with the ability of self-healing.

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Figure captions

FIG. 1. (Color online) Illustration of (a) the original and (b) fractured GaAs NWs, where two fractured surfaces with oppositely charged atoms of Ga and As atoms, are shown in (c) and (d), respectively.

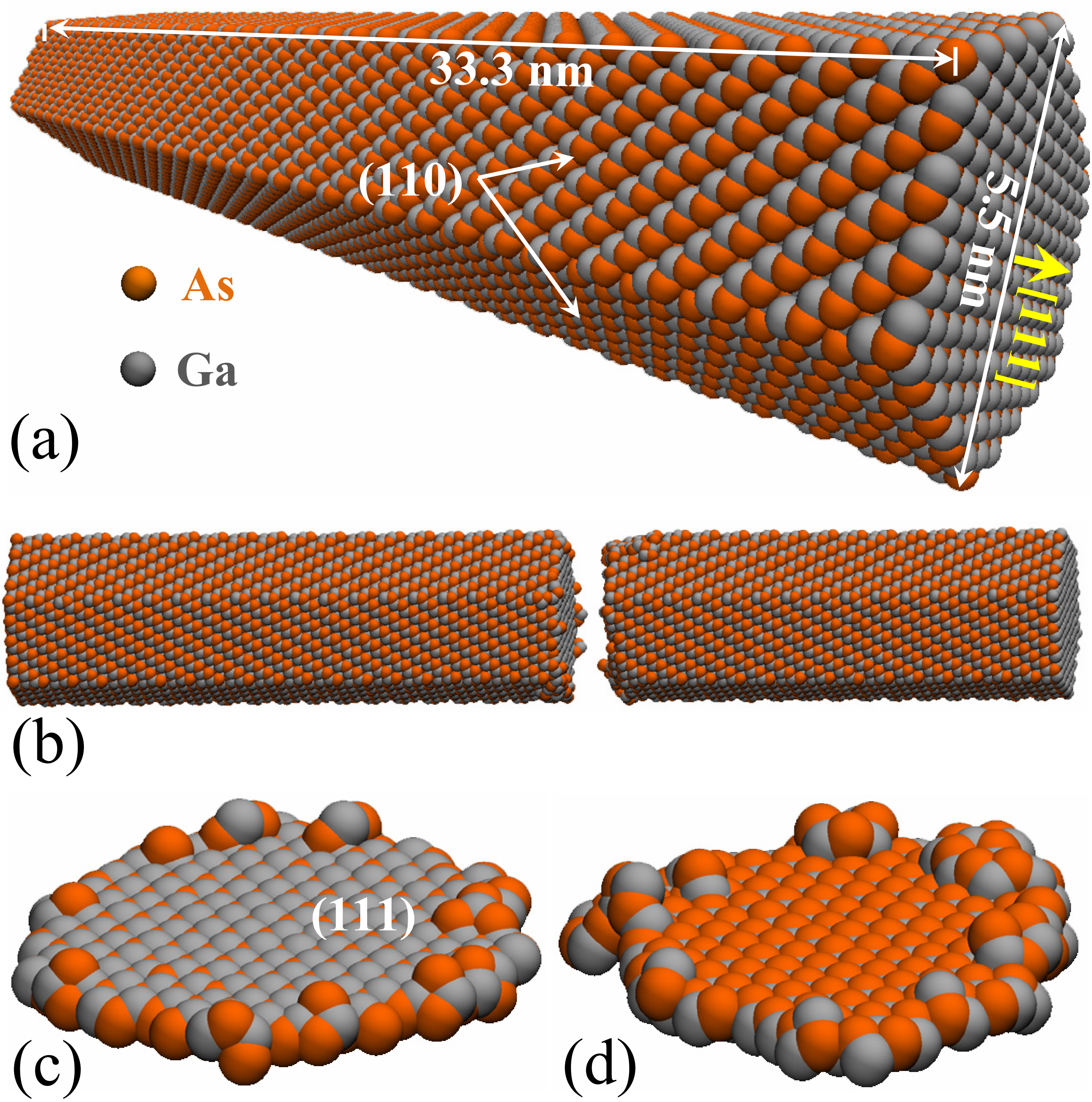
FIG. 2. (Color online) Self-healing of a fractured GaAs NW. (a) The three-stage healing process: attaching, contacting and healing. Insets are patterns at two peaks (A and B) in the healing stage. (b) Snapshot in the contacting stage, where one Ga–As bond is formed to connect two fractured surfaces (see arrow in inset). (c) The self-healed GaAs NW shows a scar on surface.

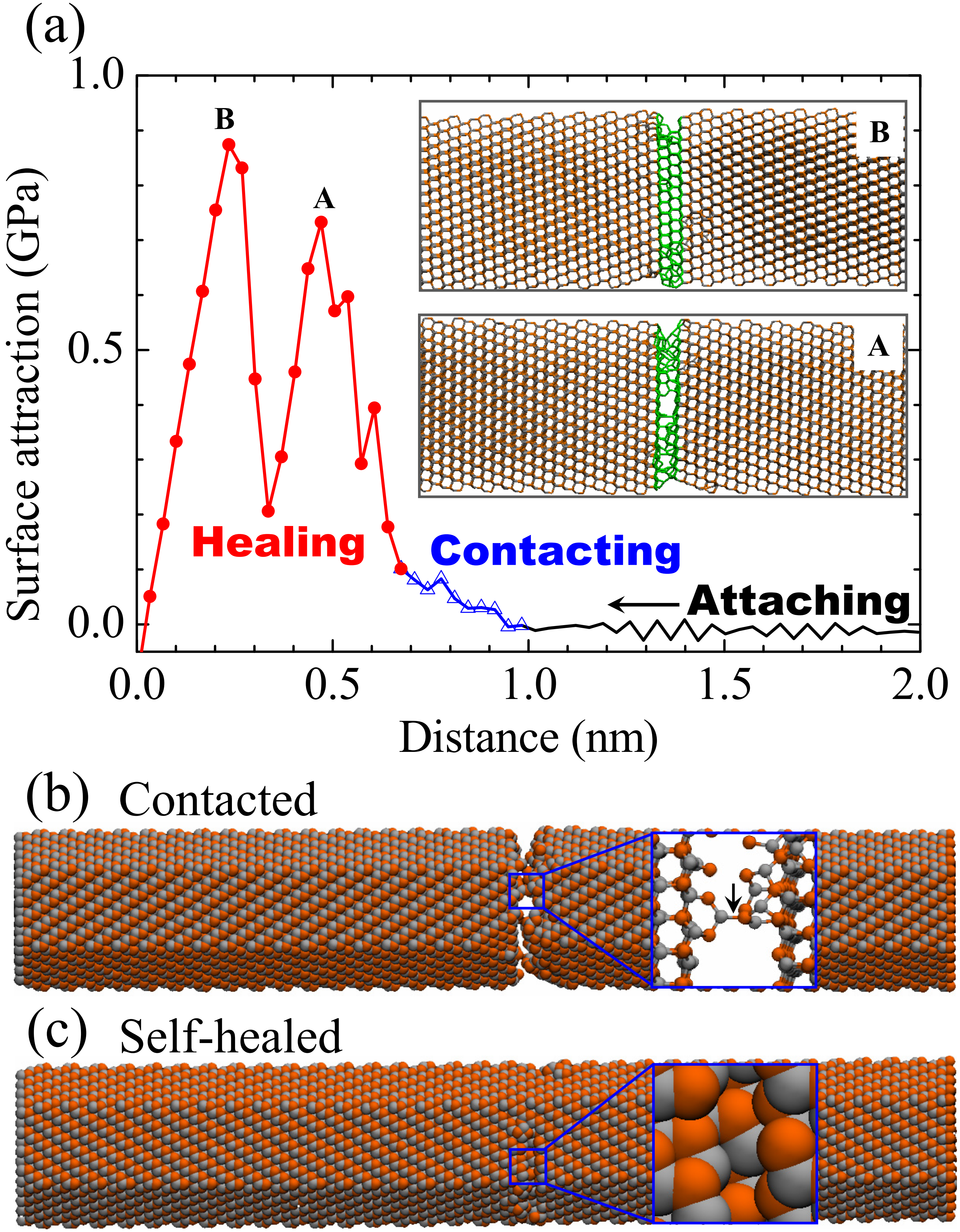
FIG. 3. (Color online) Stress versus strain curves of the virgin and self-healed GaAs NWs.

FIG. 4. (Color online) Reduced healing efficiency due to repeated cycles of fracture and healing at a reduction rate of 3.43% per cycle. The dashed line is a visual guide for the trend.

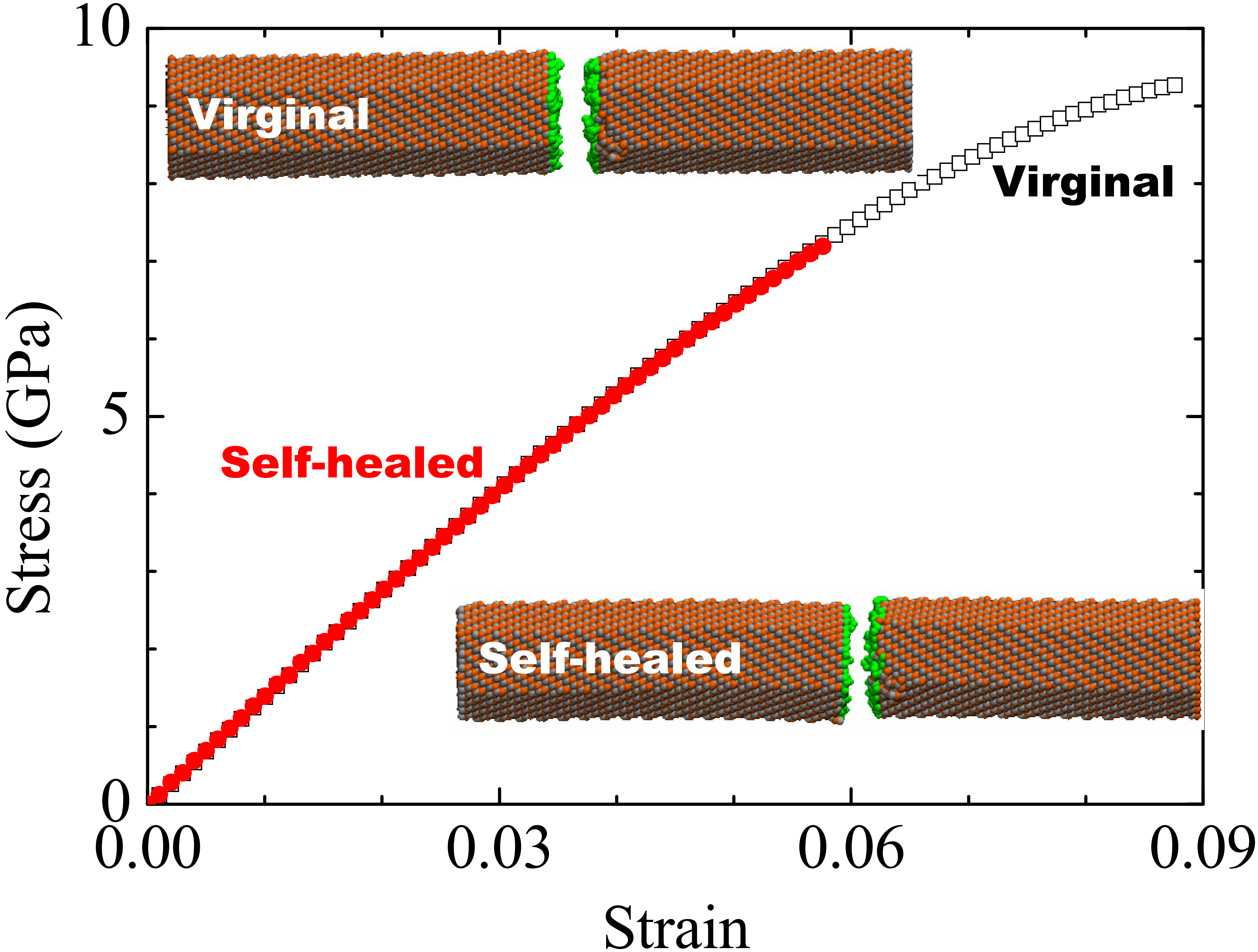
TABLE I. Self-healing of various one-dimensional nanomaterials at 300 K. CNT indicates a (37, 37) armchair single-walled carbon nanotube. All NWs have similar lateral dimension and aspect ratio as the GaAs NW under present study. For the convenience of comparison, the values of surface attraction are normalized with respect to the corresponding tensile strength of the virgin material (in the unit of GPa).

Parameter	GaAs	SiC	ZnO	GaN	CNT
Fracture surface	(111)	(111)	(0001)	(0001)	–
Virginal strength	9.27	28.53	12.57	20.81	1147.47
Restored strength	7.19	12.45	2.62	2.30	251.66
Surface attraction (%)	9.4	9.1	2.3	2.0	–
Healing efficiency (%)	77.6	43.7	20.9	11.1	21.9

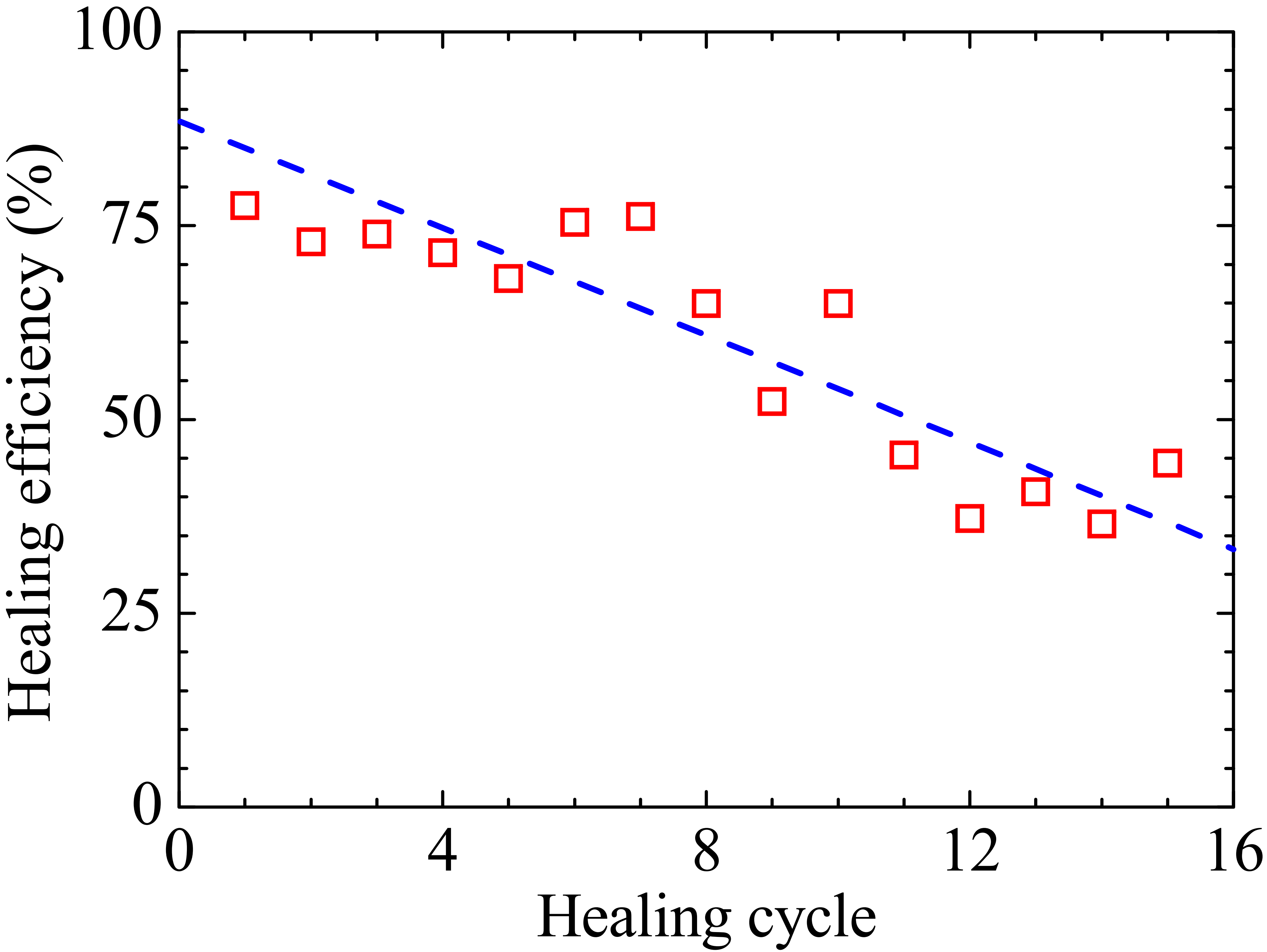

33.3 nm
(110)
As
Ga
5.5 nm
[111]
(a)
(b)
(111)
(c)
(d)



(a)
1.0
0.5
0.0
Surface attraction (GPa)
B
A
Healing
Contacting
Attaching
0.0
0.5
1.0
1.5
2.0
Distance (nm)
(b) Contacted
(c) Self-healed



Virginal
Virginal
Self-healed
Self-healed
Stress (GPa)
Strain
0
5
10
0.00
0.03
0.06
0.09


100
75
50
25
0
0
4
8
12
16
Healing efficiency (%)
Healing cycle