# Nanoscale wear as a stress-assisted chemical reaction

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Wear of sliding contacts leads to energy dissipation and device failure, resulting in massive economic and environmental costs<sup>1</sup>. Typically, wear phenomena are described empirically<sup>2</sup>, because physical and chemical interactions at sliding interfaces are not fully understood at any length scale. Fundamental insights from individual nanoscale contacts are crucial for understanding wear at larger length scales<sup>3</sup>, and to enable reliable nanoscale devices, manufacturing and microscopy<sup>4-6</sup>. Observable nanoscale wear mechanisms include fracture<sup>7</sup> and plastic deformation<sup>8</sup>, but recent experiments<sup>9-11</sup> and models<sup>12</sup> propose another mechanism: wear via atom-by-atom removal ('atomic attrition'), which can be modelled using stress-assisted chemical reaction kinetics<sup>13</sup>. Experimental evidence for this has so far been inferential. Here, we quantitatively measure the wear of silicon-a material relevant to small-scale devices<sup>14</sup>-using in situ transmission electron microscopy. We resolve worn volumes as small as  $25 \pm 5 \text{ nm}^3$ , a factor of  $10^3$  lower than is achievable using alternative techniques<sup>15,16</sup>. Wear of silicon against diamond is consistent with atomic attrition, and inconsistent with fracture or plastic deformation, as shown using direct imaging. The rate of atom removal depends exponentially on stress in the contact, as predicted by chemical rate kinetics<sup>13</sup>. Measured activation parameters are consistent with an atom-by-atom process<sup>17</sup>. These results, by direct observation, establish atomic attrition as the primary wear mechanism of silicon in vacuum at low loads.

The Archard wear equation, developed in 1953<sup>18</sup>, states that the volume removed due to wear is directly proportional to both the applied load and the distance slid. It is widely applied to macroscale (for example, ref. 19) and even microscale systems (for example, ref. 16). Although its form can be derived from simple arguments based on fully plastic material removal<sup>18</sup>, this equation is purely empirical, with no method to predict the proportionality constant. Recently, Gotsmann and Lantz performed sliding studies using an atomic force microscope (AFM) and measured changes in tip-sample adhesive forces as an indicator of tip wear; their results suggested the failure of the Archard equation for nanoscale contacts<sup>10</sup>. A robust, widely applicable replacement has not yet been established, but several experimental investigations, including ref. 10, suggest that wear occurs via atom-by-atom removal of surface material through stress-assisted bond formation and breaking. Molecular dynamics simulations<sup>12</sup> and analytical models<sup>20</sup> have supported this picture. An atom-by-atom wear mechanism assumes a unit process where individual atoms undergo chemical bonding reactions across the interface. The rate of atom loss due to wear,  $\Gamma_{\rm atom-loss}$  (units  $s^{-1}),$  is then predicted to obey reaction rate theory  $^{13}$  according to  $^{21}$ 

$$\begin{split} \Gamma_{\text{atom-loss}} &= \Gamma_0 \exp\left(-\frac{\Delta G_{\text{act}}}{k_{\text{B}}T}\right) \\ &= \left\{\Gamma_0 \exp\left(-\frac{\Delta U_{\text{act}}}{k_{\text{B}}T}\right)\right\} \exp\left(\frac{\sigma \Delta V_{\text{act}}}{k_{\text{B}}T}\right) \end{split} \tag{1}$$

where  $\Gamma_0$  is a pre-factor (an effective attempt frequency),  $k_{\rm B}$  is Boltzmann's constant, and T is the absolute temperature. The free energy of activation  $\Delta G_{\rm act}$  is reduced by the mechanical work done on the system (due to straining of bonds), and is expanded as  $\Delta G_{act} = \Delta U_{act} - \sigma \Delta V_{act}$ , where  $\Delta U_{act}$  is the internal energy of activation (the stress-free activation barrier),  $\sigma$  is the stress component that lowers the energy barrier, and  $\Delta V_{act}$  is termed the activation volume. Strictly, the activation volume is a tensor quantity with six independent components, corresponding to the dependence of the barrier height on the six independent components of stress. However, in many cases, one stress component will have the dominant effect and therefore the kinetics can be well-captured with a single stress component and a scalar value for  $\Delta V_{act}$ . The particular stress component of interest may vary depending on the pair of materials, geometry, force and so on. Furthermore, wear is likely to occur through a sequential, multi-step process (as discussed later); however, the overall rate of wear (equation (1)) will be determined by the kinetics of the slowest (or 'rate-limiting') step. Thus, in this picture, the Archard equation is replaced by an exponential dependence of wear on a single stress component, as has indeed been observed in several studies (for a review see ref. 22). However, direct experimental observation of the wear mechanisms is still lacking. Specifically, experimental evidence for the above wear law requires a demonstration that (i) nanoscale wear occurs through a gradual (atomic-scale) interfacial process; (ii) the measured kinetics directly satisfy equation (1); and (iii) the extracted activation parameters are consistent with atom-by-atom chemical reactions.

In the present study, nanoscale wear tests were conducted inside a JEOL 2010F transmission electron microscope (TEM) with a field-emission electron source, using an *in situ* nanoindentation apparatus (PI-95, Hysitron). A nominally flat (100)-oriented diamond punch was brought into contact with a series of sharp (R < 20 nm) asperities (single-crystal silicon, initially terminated with silicon oxide). The asperities in this case are the ends of AFM tips, which are integrated with microcantilevers (PPP-CONTR, Nanosensors), the deflection of which allows us to sensitively measure the applied force (Fig. 1). The diamond punch was then slid laterally, with reciprocating strokes typically of length 100 nm, and only the adhesive force acting (that is, no additional

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**Figure 1 | A modified** *in situ* indentation apparatus is used for the sliding tests. **a**, An AFM probe is mounted on the sample surface of a TEM nanoindenter. **b**, The flat punch indenter tip is brought into sliding contact with the nanoscale asperity, allowing *in situ* characterization of the evolving interface. Observing the deflection of the tip/cantilever enables the applied normal force to be determined.

applied load). The contact was separated at varying intervals throughout the wear test to measure the instantaneous adhesive force, determined by observing the tensile deflection of the calibrated<sup>23</sup> cantilever upon separation. Four different silicon tips of varying shape were tested, with total sliding distances ranging from 200 nm to 4.5  $\mu$ m for each. All sliding was recorded with real-time video (for an example see Supplementary Movie), and high-resolution (silicon lattice-resolved) TEM images of the asperities were taken at each separation. In post-processing, the instantaneous asperity profile was traced using these out-of-contact images. The profiles were then integrated to give three-dimensional shapes (assuming axisymmetry of each differential slice) to quantify the volume removed, and consequently the number of atoms removed. More detail on the experimental technique and the calculation of volume lost can be found in the Supplementary Methods.

This in situ methodology has the advantage of providing highresolution measurements of contact forces, sliding distances and the interfacial geometry, thereby allowing dynamic, quantitative visualization of the volume removed due to wear. Most previous advances in wear studies relied on stand-alone AFM instruments without in situ imaging. In those experiments, the tip-sample forces were precisely controlled, but no information was directly collected about the evolving asperity geometry (upon which the contact stresses strongly depend) or the wear mechanism itself. Owing to the inherent limitations of the AFM, asperity shape information had either to be inferred (for example, from pull-off measurements combined with assumptions about asperity shape<sup>10,11</sup>, or using blind tip reconstruction<sup>7</sup>) or captured after the fact (for example, using periodic ex situ electron microscopy<sup>15,16</sup>). These techniques achieved a volume resolution as small as  $1 \times 10^5$  nm<sup>3</sup>. Impressive tribological studies have been conducted using *in situ* TEM<sup>24</sup>. However, these involved limited sliding distances (tens of nanometres) and lacked direct force measurement. The present experiments combine sub-nanonewton force resolution,

volume resolution as low as 5 nm<sup>3</sup> and sliding increments as small as 50 nm, enabling an unprecedented view of wear on the nanoscale.

A fundamental wear model requires a clear description of the process by which material is being removed. In this study, the removal mechanism can be identified using the high-resolution out-of-contact images taken at various points throughout the wear test. The traced profiles (for example, Fig. 2a) demonstrate that the wear is gradual and uniform, with the tip surface eroding by small amounts often 1 nm or less. This is not consistent with fracture, which is sudden and irregular, and should occur along preferred crystallographic orientations. All traced profiles for the four probes are shown in Supplementary Fig. S3. Fracture can be ruled out in all cases where the wearing material is silicon. Note that the one observed instance of fracture (orange arrow, Supplementary Fig. S3b) occurred during the wearing away of the outermost oxide, and thus does not affect the quantitative analysis of the wear of silicon presented in this Letter. Additionally, the lattice-resolved images of the asperity (for example, Fig. 2b) consistently show perfect crystallographic order in the silicon, even very close to the contact interface, ruling out sub-surface plastic deformation. Once the oxide is removed (as in Fig. 2b), the lattice without defects is observed to extend to within 1 nm of the surface. Accordingly, there is significant asperity wear, occurring gradually and progressively without fracture or plastic deformation, so this material removal is directly consistent with the atomic attrition model.

The volume lost for all four AFM probes was quantified throughout the wear tests as described above, and plotted versus the cumulative distance slid (Fig. 3a). The volume removal rate (local slope from these data points) varied widely both for a given asperity and also among the four asperities. Traditionally, following Archard's law, the volume lost in a single sliding interval of a wear test is plotted versus the product of sliding distance for that interval and the total normal load (in this case, adhesive force). Although Archard's law is macroscopic in nature, for illustration purposes the data are presented in this way in Fig. 3b. The individual data sets are clearly nonlinear with a large degree of scatter, and the Archard equation fails to describe the behaviour. Furthermore, widely divergent values are seen between the four asperities, so no fundamental insight about wear is gained through this presentation of the data.

The experimental data were next analysed in the context of reaction rate theory—equation (1)—by plotting the reaction rate  $\Gamma_{\rm atom-loss}$  (in s<sup>-1</sup>; the number of atoms removed per unit time in sliding contact, normalized by the number of atoms in



Figure 2 | Periodic high-resolution TEM images demonstrate gradual surface evolution without sub-surface damage. **a**, Four traces of successive profiles of one of the four asperities tested, shown at 200 nm intervals of sliding distance, overlaid on a TEM image of the asperity just after the final interval, indicated by the red trace. The profiles are aligned using features in the unworn region further up the shank of the AFM probe. Inset: detailed view of the traces, demonstrating gradual wear of the surface, often with less than 1 nm change in the asperity height per sliding interval. **b**, Representative lattice-resolved image of the same asperity shows no evidence of dislocations or defects in the sub-surface silicon lattice, even in highly worn areas.



**Figure 3 | The volume of silicon lost due to wear has been quantified and is well described using a chemical kinetics framework. a**, The cumulative volume lost due to wear is shown for tests from four AFM probes for the first 1 µm of sliding (data beyond 1 µm is excluded for clarity, but is included in the Supplementary Data). The distinct initial (pre-wear) geometries of the four different AFM tips are shown in TEM images (i-iv). These images are all displayed at a common magnification, and the shape and colour of the corresponding data point are indicated in the image. The outer oxide layer is removed by sliding before this analysis and is not included in the measure of volume lost. **b**, To conform with the Archard equation, the data from **a** can be represented as the volume lost in a single scan as a function of the product of the distance and load for that scan. This plot demonstrates that there is neither a linear relationship between these quantities (as predicted by the Archard equation), nor is there consistent behaviour between tips. **c**, When the data for the wear of pure silicon are plotted in accordance with stress-assisted chemical reaction kinetics, the four data sets collapse to a single curve that is fit well by an exponential relationship (equation (1), dashed line). Inset: the same data collapsing to a straight line on a log-linear plot. (Note that all data are included in **c**, not just the first 1 µm of sliding.)

contact) against the mean compressive normal stress in the contact,  $\sigma_{\rm normal}$  (in Pa). It is not known  $a\ priori$  which stress component has the largest effect on the energy barrier. The mean normal stress is hypothesized here to be the controlling one for this analysis, based on the reaction pathway presented below. The atomic wear process could depend on other stress components such as the local shear stress arising from interfacial friction, as proposed previously<sup>10,11</sup>. In those earlier analyses, the interfacial shear stress was assumed to have a linear dependence on the normal stress<sup>25,26</sup>, and in such a case, equation (1) would describe the data equally well. Thus, although we propose a pathway depending on compressive normal stress, our analysis is general and applies to all mechanisms in which the energy barrier is modified by a stress component that is equal to or proportional to the compressive normal stress. Furthermore, while contact mechanics models predict that normal stresses are spatially inhomogeneous, all compressive stresses, including the peak value, scale with the mean value<sup>27</sup>. This further justifies the use of the mean normal stress for the analysis.

The mean normal stress can be calculated using the Derjaguin– Müller–Toporov (DMT)<sup>28</sup> adhesive contact mechanics model. (This is a reasonable approximation because Maugis' parameter<sup>27</sup> was calculated to be 0.17; see Supplementary equations.) In the DMT model, the total compressive force in the contact,  $F_{\text{total}}$ , is the sum of the applied load  $F_{\text{applied}}$  (zero in this case) and the adhesive load  $F_{\text{adhesive}}$ . The reaction rate and mean normal stress are calculated as follows (see Supplementary equations for more details):

$$\Gamma_{\rm atom-loss} = c \frac{V_{\rm lost}}{A_{\rm contact} t_{\rm slide}} \tag{2a}$$

$$\sigma_{\rm normal} = \frac{F_{\rm adhesive}}{A_{\rm contact}} \tag{2b}$$

where  $V_{\text{lost}}$  is the measured volume lost in the interval between high-resolution measurements,  $t_{\text{slide}}$  is the time in sliding contact

for that interval, and *c* is a constant (in m<sup>-1</sup>) that depends on the structural parameters of crystalline silicon (see Supplementary Equations).  $A_{\text{contact}}$  is the area of contact calculated by applying DMT adhesive contact mechanics<sup>27,28</sup>, with a radius extracted from a parabola fit to the outermost asperity (as shown in the Supplementary Data), determined at each interval from TEM images. This evolving asperity geometry as well as  $F_{\text{adhesive}}$  are both measured *in situ* at each interval. In the context of reaction rate theory, the time in contact,  $t_{\text{slide}}$ , is more important than the distance slid, as long as sliding is occurring. For the sliding speeds attainable in this experiment, the model predicts more atom-by-atom wear when sliding at a slower speed as there is more time for reactions to take place. To confirm this, two sliding speeds were used (4 and 21 nm s<sup>-1</sup>); both are included in Fig. 3c and the model fits both data sets equally well.

In accordance with *ex situ* studies on silicon<sup>29</sup>, wear progressed gradually through the oxide and then through the underlying single-crystal silicon. A principal advantage of performing wear tests with *in situ* imaging is the ability to distinguish the wearing materials and the wear mechanisms. Therefore, only the wear of silicon is included in the quantitative reaction rate analysis— any sliding involved in removing the oxide was excluded, including the single observed fracture event of silicon oxide (indicated in Supplementary Fig. S3b). There was no observable contamination on the surfaces of the tips. Any initially present contamination would have been removed along with the oxide.

The analysis demonstrates that an exponential dependence of reaction rate on compressive stress (Fig. 3c) clearly fits the data, consistent with the stress-assisted chemical kinetics model (equation (1)). The data for all four silicon asperities, despite their widely varying geometries, collapse consistently onto a single curve, which is nearly linear on a log-linear plot (Fig. 3c, inset). The data are extremely well fit by equation (1) (correlation coefficient of 0.90) using  $\Delta V_{\rm act}$  and  $\Delta U_{\rm act}$  as fit parameters. Accounting for experimental uncertainty and reasonable attempt frequencies

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Figure 4 | A proposed mechanism of nanoscale wear by stress-assisted atom-by-atom removal. **a**, A sharp silicon asperity in adhesive contact with a diamond substrate slides in quasi-static equilibrium relative to the substrate. **b**, One of the low-coordinated atoms from the asperity surface forms a covalent bond (green) to one or more substrate atoms. This thermally activated bond formation is facilitated by the compressive stress in the contact. **c**, The bonds to the tip are then broken as the asperity slides on, leaving a silicon atom on the substrate.

corresponding to atomic vibrations  $(1 \times 10^{14\pm 1} \text{ s}^{-1})$ , the fit yields  $\Delta V_{act} = 6.7 \pm 0.3 \text{ Å}^3$  and  $\Delta U_{act} = 0.91 \pm 0.06 \text{ eV}$ . These values are of the correct order for single-atom dimensions and bond energies, and are consistent with quantum-mechanical predictions for stressassisted chemical reactions in silicon<sup>17</sup>. The energy barrier compares favourably to the value previously measured (0.98 eV) using indirect measurements of wear for a silicon tip sliding on a polymer surface<sup>10</sup>. However, the measurements of activation volume cannot be compared directly in a meaningful manner. In ref. 10, the interfacial shear stress was assumed to be the rate-controlling stress component, and to scale linearly with compressive stress (with proportionality constant  $\xi$ , as shown in equation (3) of ref. 10). The best-fit value extracted was  $\xi \Delta V_{\text{act,shear stress}} = 55 \pm 35 \text{ Å}^3$ . Comparing that activation volume to the present one is complicated by the fact that  $\xi$  is unknown and the silicon–polymer shear stress occurring in dry air or nitrogen for the experiments in ref. 10 will differ greatly from the diamond-silicon shear stress in vacuum in the present tests. Several other differences, including assumptions about the tip geometry as it evolves, the assumption of direct proportionality between the pull-off force and the radius of the flattened tip, and different sliding speeds, render it uninformative to compare these activation volumes directly. Further experimental and simulation work is needed to identify the specific stress components responsible for reducing the relevant energy barrier in a particular set of conditions.

The specific unit process(es) leading to wear remain undetermined, as the present in situ methodology does not resolve the behaviour of individual atoms. One feasible process is a two-step mechanism (Fig. 4), where an asperity atom first forms a covalent bond across the interface, then the bonds that formerly held that atom to the asperity are broken (in a manner akin to that observed in an atomistic simulation of diamond-like carbon sliding over diamond<sup>12</sup>, for example). The non-bonded repulsion barrier that prevents covalent bonding (explicitly discussed in ref. 30) is reduced by the compressive stress in the contact, and is overcome by thermal activation. In this picture, the second step (bond breaking) usually follows after the first step (bond formation). The ratelimiting reaction for wear is therefore hypothesized to be the formation of the bond across the interface, so the extracted activation parameters describe the kinetics of this reaction. The values obtained here are consistent with this picture. There are certainly many secondary events including re-transfer of material back to the tip, surface reconstruction, diffusion, removal of groups of atoms, and so on, but the clear single-exponential behaviour seen in Fig. 3c suggests that one mechanism dominates and controls the rate of wear.

There are two major advances in the present investigation. First, the *in situ* nature of this testing provides direct experimental evidence that significant nanoscale wear can occur in the absence of fracture or plastic deformation. This implies that atomic attrition can be quite significant in nanoscale contacts, and is potentially a substantial wear mechanism at the micro/macroscale, even in brittle or ductile materials that fail by other means at higher stresses. Second, the atomic reaction rate has been directly calculated and plotted versus contact stress, explicitly demonstrating an exponential dependence over decades of reaction rate. This provides direct experimental validation of an atom-by-atom wear mechanism, and justifies the application of reaction rate kinetics in the analysis and prediction of some types of nanoscale wear. More broadly, when wear is being studied for a new set of materials or conditions, Fig. 3c provides an example of the analysis that can be performed to determine whether reaction rate theory is appropriate. Reliable values for the kinetic parameters from that analysis could then be used to predict wear for different loads and tip geometries.

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#### Author contributions

T.D.B.J. designed the test set-up, performed all testing and developed analysis routines. R.W.C. supervised the research and oversaw the analysis. Both authors prepared the manuscript.

## Additional information

Supplementary information is available in the online version of the paper. Reprints and permission information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to R.W.C.

## **Competing financial interests**

The authors declare no competing financial interests.