

# Ultralow nanoscale wear through atom-by-atom attrition in silicon-containing diamond-like carbon

Harish Bhaskaran<sup>1\*†</sup>, Bernd Gotsmann<sup>1</sup>, Abu Sebastian<sup>1</sup>, Ute Drechsler<sup>1</sup>, Mark A. Lantz<sup>1</sup>, Michel Despont<sup>1\*†</sup>, Papot Jaroenapibal<sup>2†</sup>, Robert W. Carpick<sup>2</sup>, Yun Chen<sup>3†</sup> and Kumar Sridharan<sup>3</sup>

**Understanding friction<sup>1–4</sup> and wear<sup>5–11</sup> at the nanoscale is important for many applications that involve nanoscale components sliding on a surface, such as nanolithography, nanometrology and nanomanufacturing. Defects, cracks and other phenomena that influence material strength and wear at macroscopic scales are less important at the nanoscale, which is why nanowires can, for example, show higher strengths than bulk samples<sup>12</sup>. The contact area between the materials must also be described differently at the nanoscale<sup>13</sup>. Diamond-like carbon is routinely used as a surface coating in applications that require low friction and wear because it is resistant to wear at the macroscale<sup>14–20</sup>, but there has been considerable debate about the wear mechanisms of diamond-like carbon at the nanoscale because it is difficult to fabricate diamond-like carbon structures with nanoscale fidelity. Here, we demonstrate the batch fabrication of ultrasharp diamond-like carbon tips that contain significant amounts of silicon on silicon microcantilevers for use in atomic force microscopy. This material is known to possess low friction in humid conditions, and we find that, at the nanoscale, it is three orders of magnitude more wear-resistant than silicon under ambient conditions. A wear rate of one atom per micrometre of sliding on SiO<sub>2</sub> is demonstrated. We find that the classical wear law of Archard<sup>21</sup> does not hold at the nanoscale; instead, atom-by-atom attrition<sup>7,8</sup> dominates the wear mechanisms at these length scales. We estimate that the effective energy barrier for the removal of a single atom is  $\sim 1$  eV, with an effective activation volume of  $\sim 1 \times 10^{-28}$  m<sup>3</sup>.**

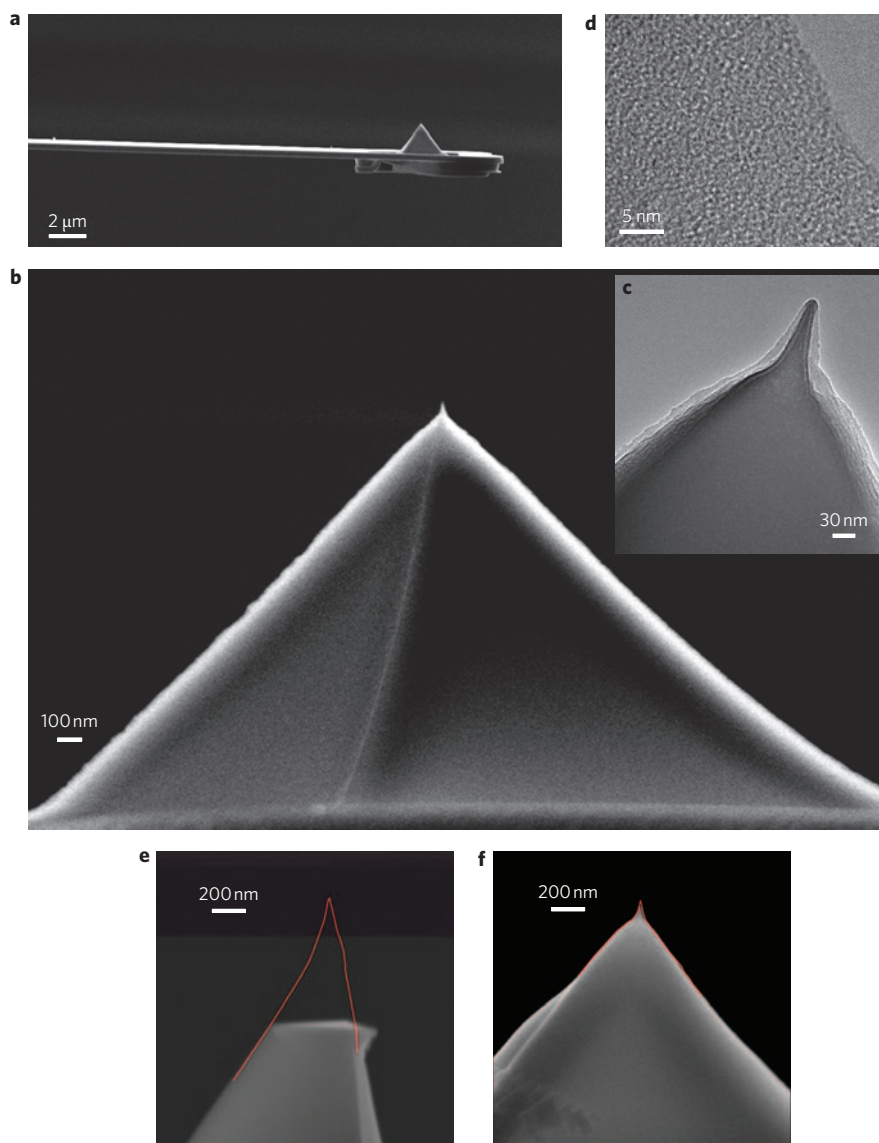
Rather than coating nanoscale tips with wear-resistant materials, we used a moulding technique<sup>22–24</sup> to fabricate monolithic ultrasharp tips of diamond-like carbon with silicon (Si-DLC) on standard silicon microcantilevers. This is a bulk processing technique that has the potential to scale up for commercial manufacturing. Because of the amorphous nature of Si-DLC and the carefully tuned plasma immersion ion implantation and deposition (PIIID) process, we achieve near complete filling of the mould (see Supplementary Information for details). This material is also expected to have significant amounts of hydrogen in addition to oxygen (31 at%) and silicon (20 at%), as measured by X-ray photoelectron spectroscopy (XPS)<sup>25</sup>.

The fabricated tips were examined in a scanning electron microscope (SEM), and one such tip is shown in Fig. 1. Transmission electron microscopy (TEM) of the tips (Fig. 1d) indicated an amorphous, homogeneous material. To image the tips for comparison of wear rates, we avoided extended electron beam exposure because of suspected beam-induced carbon deposition. This is visible in the TEM image in Fig. 1c.

The wear performance of these nanoscale tips was then evaluated for sliding wear on SiO<sub>2</sub> in an atomic force microscope (AFM). The effects of substrate wear were minimized by carefully choosing the scan pattern (see Supplementary Information). Wear was measured *in situ* as an increase in adhesion corresponding to an increase in the contact area between the tip and substrate. This was correlated to a change in tip radius using the parameter  $u_{adh}$  (see Methods). At the macroscale, wear is a result of a combination of processes including fracture, plasticity and third-body effects, as well as atom-by-atom attrition, and has traditionally been described using Archard's phenomenological model<sup>21</sup>. (Archard<sup>21</sup> describes the wear volume  $V$  of macroscopic plastic contacts with multiple asperities to be proportional to the load force  $F_N$  (not pressure) and sliding distance  $d$ , which can be written as  $V = k_{wear} \cdot F_N \cdot d$ , where  $k_{wear}$  is the dimensional wear coefficient. Bhushan later developed a similar law for elastic contacts<sup>29</sup>.) However, at the nanoscale, careful studies have shown that wear can also occur in a smooth and gradual manner<sup>9,26</sup>. This has been difficult to quantify until recently, when it was shown that this gradual wear process, at small size scales, is eventually limited to what is necessarily atom-by-atom attrition<sup>7</sup>.

Even at the nanoscale, tip wear is not necessarily limited by the strength of the atomic bonds in the material, for example, Si–Si bonds in silicon or Si–N bonds in silicon nitride, which have bond energies of up to 2.25 or 3.3 eV, respectively. Under ambient conditions, the silicon or silicon nitride surfaces terminate in a native oxide. The Si–O–Si bonds thus formed are weakened in the presence of water (hydration due to humidity such as from atmospheric humidity), and these weakened bonds are broken during the wear process<sup>7,27</sup>. Sharp tips that slide on a flat surface (such as the tips in our experiments) are ideal for studying wear mechanisms in single-asperity nanoscale contacts, where the behaviour could be considerably different. A material that compares favourably with silicon under such conditions would have substantial applications, as sliding under such ambient conditions is very important for many applications of AFM tips (and for nanoelectromechanical systems (NEMS) in general). Our wear experiments using silicon tips sliding against SiO<sub>2</sub> result in extremely high wear rates (see Fig. 1e and Supplementary Fig. S2 for wear in silicon tips). Similar wear mechanisms due to the high silicon content in Si-DLC could adversely affect the nanoscale wear of the Si-DLC tips sliding on SiO<sub>2</sub>. The study in ref. 28 suggests the presence of an oxygen-terminated surface on Si-DLC, which is consistent with our XPS measurements. Therefore, in spite of the well-known tribological properties of Si-DLC at the macroscale, it was not readily clear whether Si-DLC tips would indeed be superior to silicon tips at the nanoscale.

<sup>1</sup>IBM Research - Zurich, 8803 Rüschlikon, Switzerland, <sup>2</sup>Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, 220 South 33rd Street, Philadelphia, Pennsylvania 19104, USA, <sup>3</sup>Department of Engineering Physics, University of Wisconsin, 1500 Engineering Drive Madison, Wisconsin 53706, USA; <sup>†</sup>Present address: Yale University, Department of Electrical Engineering, 15 Prospect Street, New Haven, Connecticut 06511, USA (H.B.); Khon Kaen University, Industrial Engineering Department, Muang Khone Kean, Thailand 40002 (P.J.); Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506, USA (Y.C.). \*e-mail: bharish@umd.edu; dpt@zurich.ibm.com



**Figure 1 | Ultrasharp Si-DLC tips.** **a**, SEM image of a silicon microcantilever with an ultrasharp Si-DLC tip. **b**, Close-up of the moulded tip. **c,d**, TEM images of the apex of the tip (**c**) and an edge near the apex region (**d**), showing a homogeneous amorphous structure. **e,f**, SEM images of a silicon tip (**e**) and a comparable Si-DLC tip (**f**) under similar loading and environmental conditions after 2 m of sliding wear on a  $\text{SiO}_2$  surface. The red outline shows the tip shape before the wear experiment.

Figure 2a,c,e shows electron micrographs of three worn Si-DLC tips, with the outlines of the unworn tips (tips A, B and C) indicated by lines. From the tip images obtained in a SEM before and after wear, we estimate the wear volumes in Si-DLC to have an average value of  $\sim 8.2 \times 10^3 \text{ nm}^3 \text{ m}^{-1}$  (averaged over six wear experiments), which is almost four orders of magnitude better than the wear volumes in silicon tips, which were  $> 1 \times 10^8 \text{ nm}^3 \text{ m}^{-1}$  for similar sliding conditions (see Fig. 1e as well as Supplementary Fig. S5). The experimental parameters for the different wear experiments using the Si-DLC tips are summarized in Table 1.

Figure 2b,d,f shows the experimental wear data and fits for both Archard's law and the atomistic attrition model described below (as adapted from ref. 7). From the experimental data of the change of adhesion during sliding wear for the three tips in Fig. 2, it is apparent that the adhesion values change gradually, even over a large sliding distance. This indicates that there is a continual change in tip shape, consistent with the notion of an atom-by-atom wear process. However, the adhesion force is greatly influenced by there being a non-ideal surface, such as when wear debris or

contamination is present. This appears to be an issue for tip B after sliding for 0.5 m. Hence, for that particular experiment we restrict the subsequent analysis to the initial 0.5 m of sliding. The value of  $u_{\text{adh}}$ , which relates the contact area (which is proportional to the tip radius) to the pull-off force, was determined to be  $2.2 (+0.2/-0.1) \text{ N m}^{-1}$  from four tips for which a high-quality image was obtained after wear, so that the contact area could be determined accurately. Assuming a slow atom-by-atom wear process, note that, from ref. 7, one can describe the atom-by-atom attrition process for a conical tip of shape  $R(h)$ , where  $h$  is the position along the vertical axis of the tip and  $d$  is the sliding distance, as

$$\frac{\partial R}{\partial d} = \frac{\partial R f_{\text{attempt}} b}{\partial h v} \exp\left(\frac{1}{k_B T} \{-(E_a - V_{\text{act}} \tau_0) + P \xi V_{\text{act}}\}\right) \quad (1)$$

Here, the attempt frequency,  $f_{\text{attempt}}$ , is due to phononic vibration, and the activation energy  $E_a$  is the energy required to break the bond in question, which is reduced by the sliding-induced shear





