Response to Comment on "Synthesis of Ultra-Incompressible Superhard Rhenium Diboride at Ambient Pressure"
Hsiu-Ying Chung, *et al.*
Science **318**, 1550d (2007);
DOI: 10.1126/science.1147704

Response to Comment on "Synthesis of Ultra-Incompressible Superhard Rhenium Diboride at Ambient Pressure"

Hsiu-Ying Chung,[1,2] Michelle B. Weinberger,[1] Jonathan B. Levine,[1] Robert W. Cumberland,[1] Abby Kavner,[3] Jenn-Ming Yang,[2] Sarah H. Tolbert,[1]* Richard B. Kaner[1,2]*

Dubrovinskaia *et al*. question our demonstration that rhenium diboride (ReB_2) is hard enough to scratch diamond. Here, we provide conclusive evidence of a scratch through atomic force microscopy depth profiling and elemental mapping. With high hardness, high-bulk modulus, and the ability to withstand extreme differential stress, ReB_2 and related materials should be investigated regardless of their cost, which is not prohibitive.

Dubrovinskaia *et al*. (*1*) raise a number of issues regarding our report (*2*) on rhenium diboride (ReB_2) that deserve additional attention. First, we would like to emphasize that we never claimed to be the first group to synthesize ReB_2. That honor indeed goes to La Placa and Post, to whom we gave credit in reference 16 in (*2*). However, we realized, through hardness, incompressibility, and differential stress experiments, that ReB_2 has scientifically interesting mechanical properties.

Dubrovinskaia *et al.* (*1*) express skepticism over the ability of ReB_2 to scratch diamond. They argue that the diamond scratch shown in (*2*) was actually ReB_2 deposited on the diamond surface and that proof of a real scratch would require evidence such as an atomic force microscopy (AFM) image. Here, we provide such proof. An ingot of ReB_2 ~4 mm in diameter was attached to a stylus with mounting wax. The sample was moved across a polished diamond surface using just the weight of the stylus to supply the force. Fig. 1 shows an AFM image of the resulting scratch. The depth profile indicates that the scratch is 2 μm wide, with a depth of ~230 nm. Energy dispersive x-ray (EDX) spectroscopic mapping (Fig. 1, inset) indicates that there is no detectable rhenium deposited on the surface of the diamond. We hope that this new data will end the debate as to whether ReB_2 can scratch diamond. We would further like to point out that a scratch test is not a quantitative method for determining hardness but rather a qualitative test indicating that ReB_2 has mechanical properties worthy of serious investigation.

Dubrovinskaia *et al.* (*1*) also downplay the importance of scratching diamond and make the somewhat misleading statement that "materials much softer than diamond can damage its surface." Although the statement is true, the experiments cited by Berman [reference 7 in (*1*)] result in damage to diamond by either (i) graphitization from the heat induced by a metal ball bearing rotating at speeds in excess of 100 m/s or (ii) formation of radial cracks from tungsten carbide balls applied with loads exceeding 30 N (*3*–*5*). Mechanically, these scenarios are both very different from the deliberate formation of a linear scratch on a surface. To the best of our knowledge, only four bulk materials have previously been reported to scratch diamond, all of which are regarded as superhard: cubic boron nitride, B_6O, fullerite, and diamond-like materials (*6*–*9*).

The comments made by Dubrovinskaia *et al.* do, however, raise the important issue of what it means to be superhard. At low loads, the hardness of many materials (including ReB_2) exhibit a strong dependence on load, increasing as the load decreases. This is known as the indentation size effect. For this reason, Dubrovinskaia *et al.* believe that hardness values calculated in this

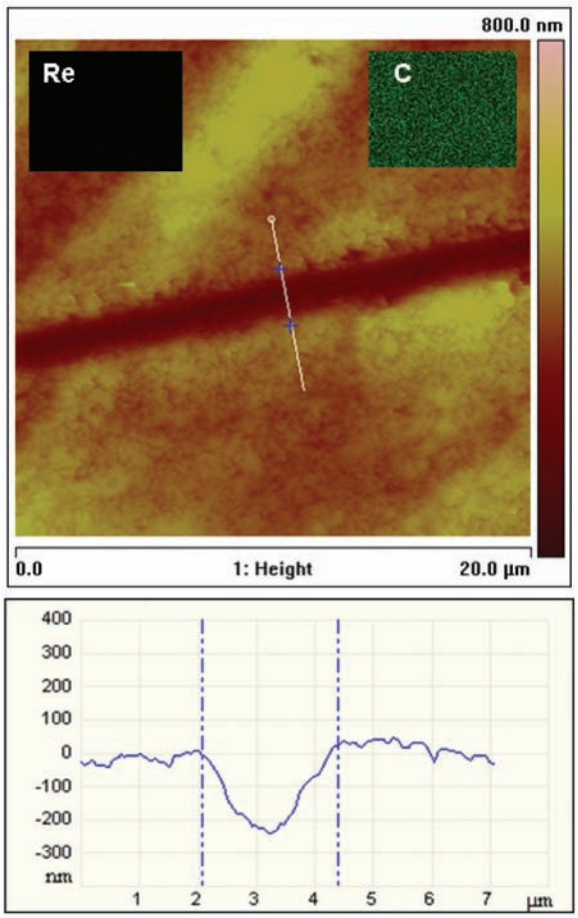

Fig. 1. An AFM image (**top**) and the corresponding depth profile (**bottom**) of a scratch made by ReB_2 on the surface of diamond. The white line follows the depth profile; the blue + s correspond to the dashed lines in the lower image. The scratch has an approximate depth of 230 nm. The insets show elemental density maps for carbon and rhenium over the entire area of the image. The green pixels in the top right inset indicate that carbon is uniformly distributed across the diamond. The absence of Re along the scratch, which should appear as red pixels in the top left inset, clearly demonstrates that ReB_2 has not been deposited on the diamond surface.

[1]Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095–1569, USA. [2]Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095–1567, USA. [3]Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095–1567, USA.

*To whom correspondence should be addressed. E-mail: tolbert@chem.ucla.edu (S.H.T.); kaner@chem.ucla.edu (R.B.K.)

regime are meaningless. The asymptotic hardness of ReB_2, with a value of 30.1 GPa, lies well below the generally accepted value of 40 GPa for superhard materials. However, other materials (e.g., transition metal borides and carbides) that have a comparable hardness to ReB_2 in the asymptotic region have not been reported to scratch diamond. Perhaps the low-load data, which achieves its maximum average hardness of 48.0 GPa at 0.49 N, in addition to the anisotropic nature of ReB_2, provide an explanation for its ability to scratch diamond. The one fact that seems clear is that until the indentation size effect is more thoroughly understood, hardness data should be collected as a function of load, and the full load dependence should be reported.

This issue leads to the more general question of how the search for superhard materials should proceed. From our work, it is clear that more than just diamond and diamond-like materials containing first row elements should be considered. Although it is not our specific priority to determine the feasibility or cost-effectiveness of a material for industrial applications, we would like to point out that Dubrovinskaia *et al.* incorrectly report the price of rhenium. At the time of this publication, rhenium metal could be purchased for approximately half the price of gold (*10*). It is clear that substituting other, less expensive transition metals for rhenium is an area that warrants future study.

Having provided clear evidence in support of our previous claims, it should be noted that Dubrovinskaia *et al*. (*11*) have demonstrated a truly remarkable method to increase the hardness of cubic boron nitride by making a nanocomposite. Because this method should be applicable to many other materials, we are now working to synthesize nanocomposites of ReB_2 in hopes of substantially increasing its hardness.

References and Notes

1. N. Dubrovinskaia, L. Dubrovinsky, V. L. Solozhenko, *Science* **318**, 1550 (2007); www.sciencemag.org/cgi/content/full/318/5856/1550c.
2. H.-Y. Chung *et al.*, *Science* **316**, 436 (2007).
3. R. Berman, Ed., *Physical Properties of Diamond* (Clarendon Press, Oxford, 1965).
4. F. P. Bowden, E. H. Freitag, *Proc. R. Soc. Lond. A* **248**, 350 (1958).
5. S. Tolansky, V. R. Howes, *Proc. Phys. Soc.* **70**, 521 (1956).
6. R. H. Wentorf Jr., *J. Chem. Phys.* **26**, 956 (1957).
7. A. R. Badzian, *Appl. Phys. Lett.* **53**, 2495 (1988).
8. V. Blank *et al.*, *Diamond Relat. Mater.* **7**, 427 (1998).
9. N. Dubrovinskaia *et al.*, *Appl. Phys. Lett.* **87**, 83106 (2005).
10. Dubrovinskaia *et al.* claim that rhenium costs nine times as much as gold, citing a Web site that simply attempts to estimate the free market price of the metal, which has no bearing on the current cost of rhenium. Rhenium metal can be purchased from Rhenium Alloys, Inc. at a price of $12/gram.
11. V. Dubrovinskaia *et al.*, *Appl. Phys. Lett.* **90**, 101912 (2007).

31 July 2007; accepted 6 November 2007
10.1126/science.1147704