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Guest Editorial: A Hunt for Ultrahard Materials

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Superhard materials (i.e. those having a load-invariant Vickers hardness $H_v \geq 40$ GPa) are widely used in many industrial applications (abrasives, cutting tool materials, wear-resistant coatings, etc.) where high hardness and shear strength, large elastic moduli, high melting temperatures and chemical inertness are of crucial importance. The Special Topic, "Ultra-Hard Materials", in *Journal of Applied Physics* advances our understanding of fundamental properties of existing superhard and ultrahard materials with the goal of rediscovering and synthesizing new ones. In a Tutorial by *Le Godec et al.*, various technological and conceptual tools for studying these materials are outlined, including an outlook on higher-pressure accessibilities, contemporary *in-situ* studies, advanced prediction from theory, and discovery of new ultrahard material precursors [1].

Vickers hardness of the vast majority of superhard materials is in the range of 40-60 GPa, i.e. does not exceed the hardness of single-crystal cubic boron nitride (for details, see Ref. 1 and references therein). Until very recently diamond was the only known material which is ultrahard. Diamond's unique properties such as extreme hardness (up to 120 GPa [2]), high thermal conductivity, wide band gap, high electron and hole mobility make it suitable for a variety of scientific and technological applications, however, it is rather reactive with oxygen and ferrous metals. Besides, hardness of diamond drastically drops with temperature, down to ~20 GPa at 1400 K [3]. Thus, growing demand for advanced materials for current and emerging needs stimulated the search for novel ultrahard materials that are more thermally and chemically stable than pure diamond.

At the end of the last century, some materials, such as 3D-polymerized fullerites [4] and hypothetical low-compressibility carbon nitrides,[5] were claimed to be harder than diamond. However, *Brazhkin and Solozhenko* clearly show this is definitely not the case [6].

At the turn of the millennium, cubic BC₂N, a ternary compound that is halfway between diamond and BN in composition has been synthesized at extreme pressure–temperature conditions [7]. The load-independent Vickers hardness of *c*-BC₂N is 76(4) GPa [8] which made it the second after diamond hardest phase and a member of the ultrahard materials family. The elastic recovery of *c*-BC₂N is 68% which is higher than that of cubic BN (60%) and approaching that of diamond. At ambient pressure in argon atmosphere *c*-BC₂N remains stable up to 1800 K, and, hence, is characterized by remarkably higher thermal stability than polycrystalline diamond with the same grain size. A year later, ultrahard

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low-compressible ($B = 420$ GPa) cubic BN-C solid solutions with stoichiometry close to BCN and statistically uniform atom distribution were synthesized by isoentropic shock compression [9].

In 2009, another ultrahard phase, diamond-like BC₅, was synthesized under high pressure – high temperature conditions [10]. This new phase corresponds to the ultimate solubility of boron in diamond and possesses Vickers hardness of 71(8) GPa, unusually high for superhard materials fracture toughness (~ 10 MPa·m^{1/2}), and very high (up to 1900 K) thermal stability which makes it an exceptional superabrasive overcoming diamond and promising material for high-temperature electronics. The beneficial combination of electrical conductivity, band structure that is uncommon for diamond-like phases due to electron deficiency of boron atoms, and high thermal stability will eventually allow the expansion of the boundaries of high-power electronics at extreme conditions.

It should be noted that diamond-like BC₅ and cubic BC₂N are metastable phases and can be synthesized only in the relatively narrow temperature ranges under pressures of ~ 20 GPa which makes their production quite a challenge. Superhard and ultrahard ternary B–C–N structures of other stoichiometries (such as BC₆N [11] and BC₈N of *Gao et al.* [12]) have been predicted from first-principles studies, but none of them have ever been synthesized.

The ultra-hardness can be also achieved extrinsically by creation of nanostructures and/or nanocomposites that leads to significant increase of the material hardness, mainly due to the grain-boundary strengthening (Hall–Petch effect) (see *Brazhkin and Solozhenko* [6] and references therein).

In 2003, synthesis of nanocrystalline diamond by direct solid-phase transformation of graphite at pressures above 12 GPa and high (2600–2800 K) temperatures was reported [13]. Knoop hardness of such nanocrystalline bulks reached 140 GPa, which is significantly higher than that of single-crystal diamond. Aggregated diamond nanorods synthesized by direct transition of C₆₀ fullerite at 20 GPa and 2500 K were claimed to be the densest and least compressible form of carbon [14]. Nanotwinned diamond with claimed Vickers hardness up to 200 GPa was recently synthesized at 20 GPa and 2200 K from onion carbon nanoparticles [15], however, such unprecedented hardness should be considered highly questionable [6]. In general, nano-polycrystalline diamond materials (irrespective of the precursor; e.g. graphite, fullerenes, carbon nanotubes, soot) are ultrahard and have significantly higher wear resistance and fracture toughness than single-crystal diamond. In contrast, Vickers hardness of highly polymerized 3D fullerites does not exceed 65 GPa, as shown by *Lyapin et al.* [16].

The first attempt to synthesize nanocrystalline cBN resulted in the formation of ultrahard aggregated nanocomposite of cubic and wurtzitic (wBN) polymorphs [17]. This nanostructured material has Vickers hardness above 80 GPa, but its thermal stability is relatively low due to the presence of metastable wBN. Successful synthesis of single-phase nanocrystalline cBN was performed by direct solid-state phase transformation of graphite-like BN with "ideal random layer" structure at 20 GPa and 1770 K [18]. *Solozhenko et al.* report the material shows very high hardness ($H_V = 85(3)$ GPa) and superior fracture toughness ($K_{Ic} = 10.5$ MPa·m^{1/2}) [19]; high thermal stability and oxidation resistance (up to 1500 K) have also been demonstrated [18]. Later synthesis of ultrahard nanotwinned cBN has been reported [20], however, extremely high Vickers hardness (up to 108 GPa) claimed by the authors is unjustified [21].

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Another concept for the design of novel ultrahard materials involves the formation of nanocomposites consisting of two or more nanocrystalline hard phases (e.g. TiN, VN, and W₂N) imbedded into amorphous matrix (e.g. Si₃N₄ and BN) by chemical vapor deposition (CVD), reactive sputtering or vacuum arc evaporation combined with plasma CVD [22,23]. In particular, nanocrystalline TiN/TiSi_x coatings with Vickers hardness from 80 to 105 GPa have been reported [23], however, these values seem to be overestimated.

In the last two decades, along with experimental work on synthesis of ultrahard materials, theoretical methods for predicting the mechanical properties of solids have been developed very rapidly, from empirical, but physically motivated models of hardness [24,25] and fracture toughness, including very recent works by *Mazhnik and Oganov* [26] and *Niu et al.* [27], to *ab-initio* calculations of elastic constants by *Xie et al.* [28] and *Ivashchenko et al.* [29], and, finally, to computational discovery of superhard and ultrahard materials by *Kvashnin et al.* [30]. The proposed methods have been shown to work successfully even in the case of boron-rich solids which are characterized by an extreme complexity of the crystal structure and a large number of atoms in a unit cell (*Jay et al.* [31] and others [32]). Thus, the modern evolutionary algorithms and powerful computer systems can be used to predict new structures and compounds, and to search for materials with optimal mechanical properties in order to create a "treasure map" of superhard materials. At the same time, precise calculations of mechanical properties of superhard materials (hardness, in particular) often lie beyond the capabilities of the most advanced and modern techniques. Besides, not all theoretically predicted structures exist or can be synthesized. A vivid illustration is the case of hypothetical cubic form of C₃N₄ with bulk modulus exceeding that of diamond [5]. Despite the enormous efforts (new attempts are still being undertaken, for instance, by *Gao et al.* [33]), this phase has not been synthesized so far, and its expected ultrahardness has never been demonstrated.

To summarize, we should note that the search for novel ultrahard materials is just at the cutting edge of fundamental science and promises great prospects for the creation of new technologies required for emerging applications. In particular, over the past decade, nanodiamonds have progressed to fully functioning materials that can be used for a wide range of applications. Recent achievements in the field clearly indicate that synthesis of phases with hardness exceeding that of diamond is very unlikely (or even impossible [6]). Rather than harder, we have to consider the possibility to synthesize (or design) materials that are more useful than diamond, e.g. more thermally and chemically stable, and harder than cubic boron nitride.

As Guest Editors, we do hope that the Special Topic: Ultra-Hard Materials will help the readers to gain a better understanding of the subject, the current trends and problems in the field, and will inspire the readers to generate new ideas on creation and design of novel superhard and ultrahard materials. We would like to thank the authors for their contributions and editors of the *Journal of Applied Physics* for coordinating the Special Topic.

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