# **New Routes in the Preparation** of Mechanically Hard Films

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Superhard nitride superlattice coatings with nanometer-scale multilayers have hardnesses exceeding 50 gigapascals, making these films highly resistant to abrasion. The nitride superlattice films can be deposited economically by reactive sputtering in production-size equipment on a variety of substrates. A model for the superlattice strength enhancement has been developed that accurately predicts which materials can be used together to produce the enhanced hardness. Advancements in sputtering technologyspecifically, pulsed dc power and reactive-gas partial-pressure control-make it possible to reactively deposit nonconducting oxide films at high deposition rates. This technology is being used along with the superlattice strength model in the development of oxide superlattice films.

Hard coatings such as titanium carbide (TiC), titanium nitride (TiN), and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) have been used successfully since the early 1970s to enhance the life of cutting tools and many other components for which friction and wear are a problem. Thin coatings of these materials on the order of 5 µm with hardnesses of about 20 GPa are effective in extending tool life by factors of 4 to 20, depending on the cutting conditions. Although the hardness of the film is a key property of the coating, particularly in abrasive cutting conditions, the chemical inertness of the film with respect to the material being machined is also important.

The use of hard coatings has spread well beyond tools; today, hard coatings are used for many tribological applications, such as on bearings or cams, and for decorative or functional coatings, such as on pens, door knobs, or faucets. For rolling elements such as bearings, standard 5-µm tool coatings can actually be deleterious, whereas much thinner coatings (on the order of 0.5 to 0.75 µm) can enhance the life of rolling elements six- to eightfold (1).

Decorative coatings on items like pen barrels or hardware must be not only attractive but functional, with many of the properties of tool coatings. For example, coatings on pens need to be hard enough to withstand the abrasive wear that occurs in pockets and purses, and they must be well adhered to the substrate material to prevent chipping or flaking when dropped on the floor. Corrosion is also a serious problem for most decorative coatings. Writing instruments must withstand highly corrosive human perspiration, and exterior door handles must stand up to the elements in addition to regular handling. All of these requirements are met by hard coatings such as TiN or zirconium nitride (ZrN). They not only have an appealing golden color but are also very hard and resistant to wear and corrosion.

Oxides such as  $Al_2O_3$  are much more stable in air at high temperatures than are nitrides. During high-speed machining, the temperature at the tip of the tool can reach 1000°C. An Al<sub>2</sub>O<sub>3</sub> coating on a tool protects it from the chemical dissolution that occurs between the tool material and the chip at these temperatures. Unfortunately, oxides lack the strength that nitrides have to withstand the mechanical abuse of cutting. To be successful, the oxides are frequently used in multilayer coatings, with either TiN or TiC. This combination provides both high strength and chemical inertness. The individual layer thicknesses are on the order of 0.5  $\mu$ m, and the overall thickness of the multilayer films is 5 to 10  $\mu$ m.

Although the early hard coatings were applied by chemical vapor deposition at temperatures around 1000°C, the need for lower temperature deposition conditions has led to the successful development of physical vapor deposition (PVD) hard coatings, which can be deposited at temperatures less than 500°C. Although the PVD technology encompasses both evaporation and sputtering, magnetron sputtering is used almost exclusively today. The lower PVD deposition temperatures are very important for the tool industry because steel for high-speed tools maintains its hardness only to temperatures around 550°C. As industries adopt more and more functional coatings for wear or corrosion protection, the ability to deposit them at temperatures as low as 150°C is becoming increasingly important. With this broader market for hard films comes a need for far greater flexibility in the engineering of their properties to meet the requirements of each application.

Nitride Superlattice Coatings The success of the early thin, hard coatings in preventing wear has led to efforts to create even better wear-resistant coatings. An important development in the quest to produce even harder coatings came from Linköping University when researchers there reported significant hardness enhancements for single-crystal nitride superlattice coatings composed of many thin, alternating layers of TiN and vanadium nitride (VN) (2). When the superlattice period (which is the bilayer thickness of two materials) was between 5 and 10 nm, the hardness of the overall coating was over 50 GPa, which is more than twice the hardness of either component material. Similar results were found at Northwestern University (3) for a TiN and niobium nitride (NbN) combination, where again the overall hardness of the superlattice coating was greater than 50 GPa.

Both the TiN/VN and TiN/NbN superlattice coatings were grown heteroepitaxially on magnesium oxide (MgO) single crystals. All three materials have the rocksalt structure, and there is lattice mismatch between the size of the three unit cells that produces strain across the interfaces between the different layers.

Even though the single-crystal nitride superlattices were very important in showing that it is possible to increase the hardness of coatings substantially, they did not relate to the everyday world very well. Few, if any, tools are made from MgO single crystals, unless of course you consider MgO as a teaching tool. To use these superhard coatings (defined as having a hardness >40 GPa) in practical applications requires that they be deposited on common polycrystalline substrate materials such as steels or cemented carbides. They must also be able to be deposited in industrial-size coating equipment at a reasonable cost if they are to be accepted as a viable commercial coating material. The science of making these superlattice coatings had been established, but the obstacle that had to be overcome was to use this science in the practical, industrial world.

Work was undertaken at Northwestern University to deposit polycrystalline nitride superlattice coatings on typical tool materials. The work was done in an opposedcathode, unbalanced magnetron sputtering system (4) (Fig. 1). There are several important features of this unit. The size of the cathode, 13 cm  $\times$  38 cm, is one that is commonly used in industry, and it is big enough to coat life-size components such as drill bits or turbine blades, which is important for demonstrating the viability of the technology on a practical scale. The substrate is rotated on a table, which must be sufficiently large to prevent any direct

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cross-contamination of sputtered material from one cathode onto the other.

For deposition of the superlattice coatings, a titanium target was mounted on one of the cathodes, and the other material (either niobium or vanadium) was mounted on the other cathode. The coatings were deposited reactively; that is, the metal targets were sputtered in an argon-nitrogen atmosphere. Automatic feedback control of the partial pressure of the reactive gas (nitrogen) was used to maintain high deposition rates and precise control of the composition of each layer (5). Because each coating material may require a different (known) partial pressure of the reactive gas to achieve stoichiometry, nitrogen was fed to each cathode independently with one flow rate slaved to the other to maintain a different partial pressure of reactive gas at each cathode (6). The superlattice period of the coating was primarily determined by the power to each sputtering cathode, the partial pressure of the reactive gas, and the speed of rotation of the substrate holder. Typical deposition rates for the superlattice coatings with 5 kW of power to each cathode, a nitrogen partial pressure of 0.03 Pa, and a negative substrate bias voltage of 150 V are 5 to 6  $\mu$ m hour<sup>-1</sup>, which is similar to the rate for traditional single-component films applied commercially.

This closed-field, unbalanced magnetron system provides a relatively dense secondary plasma in the region surrounding the substrate, and ions from this plasma are used for ion-assisted deposition of the coatings. Ion current densities on the substrate of 5 mA cm<sup>-2</sup> are typical when the power to each cathode is 5 kW and the negative substrate bias voltage is 150 V. Without this ion-assisted deposition, it is not possible to produce fully dense, well-adhered coatings in this sputtering system at low deposition temperatures.

Several different nitride superlattice coatings have been successfully deposited in the opposed-cathode sputtering system on a va-

riety of substrate materials, such as highspeed tool steel, glass, silicon, stainless steel, and cemented carbide. The coatings are polycrystalline, and depending on the choice of layer materials and superlattice period, there can be a significant increase in hardness for these polycrystalline nitride superlattice coatings. For TiN/NbN and TiN/VN polycrystalline superlattice coatings (6, 7), the peak in hardness of over 50 GPa comes at a superlattice period in the range of 4 to 8 nm (Fig. 2). These results are very similar to what was found for the single-crystal superlattice coatings. Not all combinations of nitride coatings produce an increase in hardness (Fig. 2). For the NbN/VN combination, there is little change in hardness over a wide range in superlattice periods.

The early understanding of why one pair of materials produced an increase in hardness and another did not came from the work of Mirkarimi *et al.* (8) and Shinn *et al.* (3, 9). Initially, from the study of the hardening mechanisms in the nitride superlattice films, it was postulated that coherency strain at the interface between the two layers might play a major role in enhancing the hardness of these nanometer-scale multilayer films. However, Mirkarimi *et al.* showed that the coherency strain plays only a minor role in the hardening mechanism.

Shinn et al. looked at the effect of differences in the elastic modulus of the two nitride materials. When there is a difference in modulus between the two nitrides (as there is for TiN/VN or TiN/NbN superlattice films), there is an enhancement in the hardness of the film. When there is little difference in modulus, there is little or no enhancement in hardness [for example, for NbN with an alloyed hard coating of VNbN (9) or for NbN/VN (10)]. Shinn et al. concluded that a difference in elastic modulus between the two layer materials is required to increase the hardness of the superlattice films and that the coherency strain has only a minor effect. This work on the single-crystal nitride superlattices also failed to show any evidence of the so-called "supermodulus effect" that had been reported in earlier work with metallic superlattices (11), in which the modulus of the superlattice films was greater than the rule of mixture values for the two components.

### Superlattice Hardening Model

A further insight into the hardness enhancement mechanisms in the nitride superlattice coatings came when the hardness enhancement model of Chu and Barnett (12) was published. This model is based on the restricted dislocation movement within and between layers in a superlattice film. According to the model, when the superlattice period is less than the optimum value for peak hardness, it is more difficult to move a dislocation within an individual layer than it is to move it between layers. The force needed to move the dislocation across the boundary between the layers is related to the difference in dislocation line energies or shear modulus for the two layer materials and to the width of the interface between the two layers. When the difference in shear modulus is high, the force needed to move the dislocation will be high, and this force will increase as the superlattice period increases. A point is reached when it is easier to move a dislocation within a layer than it is to move it across the boundary between the layers, and this force to move the dislocation within a layer decreases as the superlattice period increases.

The agreement between the superlattice hardening model and the experimental results is excellent (10, 12). The model predicts the peak in hardness when there is a difference in shear modulus between the two layer materials, and when the interface width is taken into account, the experimental values for hardness are close to those predicted by the model. This model provides a basis for choosing materials to achieve an increase in hardness and

Fig. 1. Schematic drawing of the opposed-cathode, unbalanced magnetron sputtering system used to deposit the polycrystalline nitride superlattice coatings.





Fig. 2. Hardness of polycrystalline superlattice films of TiN/NbN, TiN/VN, and NbN/VN as a function of the superlattice period  $\lambda$ .

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strength in a superlattice system. Two key points are that there should be a difference in shear modulus for the two layer materials and that the layers should be distinct with sharp interfaces. The model also accurately predicts that there is little increase in hardness when there is little or no difference in shear modulus for the two materials [Fig. 2, NbN/VN (10)].

### **Reactive Sputtering of Oxides**

Until just recently, reactive sputtering of oxides has been a difficult task. Oxygen reacts much, more quickly with the target surface than does nitrogen, and it often forms an insulating compound on the target surface, leading to difficulty in sputtering the material. During dc reactive sputtering, these insulating surfaces on the target build up a charge and then discharge, which results in arcing. This arcing is particularly violent for reactive dc sputtering of highly insulating oxides such as  $Al_2O_3$ , and it can result in damage to the power supply and in ejection of liquid droplets from the target surface, leading to poor-quality films.

Radio frequency (rf) power can be used for the reactive sputtering of oxides, but it has its own set of problems. Essentially half of the power is not used for sputtering, and consequently, the deposition rates for reactive sputtering with rf power are much lower than those for the pure metal. For example, the deposition rate of  $Al_2O_3$  reactively sputtered with rf power and flow control of the reactive gas is only 2 to 3% of the metal deposition rate.

Within the past few years, it has been shown (13) that bipolar pulsed dc power can be used for the reactive sputter deposition of insulating oxides. With bipolar pulsed power, the polarity of the target voltage is periodically switched from negative to positive; during the positive pulse, the charge on the oxide layer is discharged when electrons are attracted back to the positive surface. During the negative pulse, ions are attracted to the target surface, and sputtering takes place initially from all surfaces on the target, even those that have formed a compound.

Bipolar pulsed power is classified as symmetric or asymmetric, which refers to the pulse height in the positive and negative directions (14). Symmetric bipolar pulsed dc power has equal pulse heights in both the positive and negative directions, whereas asymmetric bipolar pulsed dc power has a negative pulse height that is greater than the positive one (Fig. 3). The width of the asymmetric positive pulse is usually 10 to 20% of the width of the negative one. A significant portion of the power cycle is spent in the sputtering mode, and the deposition rate

from asymmetric power can be close to that achieved with pure dc power. The frequency of pulsed dc power covers a wide range from 0 Hz (normal dc) up to 250 kHz, and typical operating frequencies for the pulsed dc power during reactive sputtering of oxides are in the 20- to 100-kHz range.

### **Oxide Superlattice Coatings**

The success with the deposition of polycrystalline nitride superlattice films and the development of the superlattice strength enhancement model has opened the way to explore other superlattice systems. Although multilayered oxide films have been used for years in the optics industry, they have not been explored as possible superlattice films with enhanced strength properties. The recent advancements in power supply technology with the introduction of pulsed dc power, combined with partial-pressure control of the reactive gas, is a new deposition tool that makes it practical to consider the deposition of oxide films at economical rates.

Aluminum oxide coatings previously had been nearly impossible to deposit using conventional dc power, and the slow deposition rates with rf power made Al<sub>2</sub>O<sub>3</sub> very expensive. Pulsed dc power has changed all of that. Schneider et al. (15) were able to deposit clear amorphous Al<sub>2</sub>O<sub>3</sub> films with excellent optical properties on a variety of substrates using the combination of pulsed dc power and partial-pressure control of the reactive gas. It is important that both techniques be combined because they complement one another to produce an extremely well-controlled process. The index of refraction for a film deposited onto a glass substrate was 1.67, which is slightly higher than the value found for the best evaporated Al<sub>2</sub>O<sub>3</sub> films. The deposition rate for clear Al<sub>2</sub>O<sub>3</sub> films formed with the use of pulsed dc power can reach 78% of the metal deposition rate, which is about 25 times that obtainable with rf power.

Other oxides are also easy to deposit now. For example, in the zirconium-oxygen system, it is now possible to deposit a complete range of films from pure Zr metal to stoichiometric  $ZrO_2$ . The oxygen content of the films can be accurately controlled



**Fig. 3.** Schematic representation of asymmetric bipolar pulsed dc power.

with partial-pressure control, and pulsed power and partial-pressure control result in a very steady process without any arcing. Deposition rates as high as 85% of the metal deposition rate can be achieved for clear crystalline  $ZrO_2$  films (16).

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The experience with the deposition of nitride superlattice films, the understanding of the model for superlattice strength enhancement, and the pulsed dc sputtering of oxides combined with partial-pressure control of the reactive gas is opening up new avenues for research. Multilayer nanometerscale oxide films composed of alternating layers of Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> have been deposited at a high rate onto glass, silicon, and high-speed tool steel substrates. These films are clear, and the structure is amorphous according to x-ray diffraction analysis. There was no radiant heating of the growing films other than that from the plasma, and the low substrate temperature during deposition, which did not exceed 300°C, was not high enough to result in a crystalline structure. Normally, ZrO<sub>2</sub> films, when deposited individually in the opposed-cathode unbalanced magnetron sputtering system, have a monoclinic crystalline structure (16), but when they combine with  $Al_2O_3$  as part of a multilayered film, the  $Al_2O_3$  sets the amorphous structure for the combined film.

Although the work on the oxide superlattices is in its infancy, the initial results are very encouraging. Energy input into the growing film in the form of heat and ion bombardment made possible by the pulsed dc power will produce crystalline films. On the assumption that the superlattice hardening model is applicable to oxides as well as nitrides, the possibility now exists to strengthen the oxide films by depositing them in a crystalline multilayer scheme. The two layer materials must have a difference in shear modulus and the interfaces between layers must be kept small. Work is currently under way to show that superhard superlattice oxide films can in fact be made. There is a need for hard, wear-resistant oxide films, and oxide superlattice coatings will quickly find uses in optical, thermal-barrier, and high-temperature applications.

### Conclusion

The combination of superlattices with high-rate oxide deposition is opening up entirely new and exciting routes for the production of hard and superhard films. The wide range of options introduced by the superlattice technology, together with the theoretical understanding of these systems, opens up the practical possibility of truly engineering surfaces, rather than simply depositing coatings.

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# Biomimetic Pathways for Assembling Inorganic Thin Films

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Living organisms construct various forms of laminated nanocomposites through directed nucleation and growth of inorganics at self-assembled organic templates at temperatures below 100°C and in aqueous solutions. Recent research has focused on the use of functionalized organic surfaces to form continuous thin films of single-phase ceramics. Continuous thin films of mesostructured silicates have also been formed on hydrophobic and hydrophilic surfaces through a two-step mechanism. First, under acidic conditions, surfactant micellar structures are self-assembled at the solid/liquid interface, and second, inorganic precursors condense to form an inorganic-organic nanocomposite. Epitaxial coordination of adsorbed surfactant tubules is observed on mica and graphite substrates, whereas a random arrangement is observed on amorphous silica. The ability to process ceramic-organic nanocomposite films by these methods provides new technological opportunities.

**B**iologically produced inorganic-organic composites such as bone, teeth, diatoms, and sea shells are fabricated through highly coupled (and often concurrent) synthesis and assembly. These structures are formed through template-assisted self-assembly, in which self-assembled organic material (such as proteins, or lipids, or both) form the structural scaffolding for the deposition of inorganic material (1). They are hierarchically structured composites in which soft organic materials are organized on length

scales of 1 to 100 nm and used as frameworks for specifically oriented and shaped inorganic crystals (that is, ceramics such as hydroxyapatite, CaCO<sub>3</sub>, SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>) (1-3). In some cases, structurally organized organic surfaces catalytically or epitaxially induce growth of specifically oriented inorganic thin films. Most importantly, however, nature's way of mineralization uses environmentally balanced aqueous solution chemistries at temperatures below 100°C. This approach provides an attractive alternative to the processing of inorganic thin films, especially in applications where substrates cannot be exposed to high temperatures, or more generally in the pursuit of increased energy efficiency.

A classic and a widely studied example of a biocomposite is the nacre of abalone shell, in which thin films of organic (<10 nm) and inorganic ( $<0.5 \mu$ m) phases are coupled together to produce a laminated structure with improved mechanical properties (4-6). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of this material are shown in Fig. 1. Because of this special architecture, composites such as nacre are simultaneously hard, strong, and tough (4-6). The core of the organic template is composed of a layer of  $\beta$ -chitin layered between "silklike" glycine- and alanine-rich proteins (7). The outer surfaces of the template are coated with hydrophilic acidic macromolecules rich in aspartic and glutamic acids (8). Recent studies suggest that these acidic macromolecules alone are responsible for control of the polymorphic form and the morphology of the CaCO<sub>3</sub> (calcite versus aragonite) crystals (9), although the role of the  $\beta$ -chitin supported matrix on the lamellar morphology of the CaCO<sub>3</sub> layers over macroscopic dimensions still remains to be determined. Morphological and crystallographic analyses of the aragonitic thin layers of nacre by electron microdiffraction show that c-axis-oriented aragonite platelets form a hierarchical tiling of a twinrelated dense film with twin domains extending over three length scales (4, 10). Superposition of the aragonite lattices on all three possible sets of twins generates a new superlattice structure, which suggests



Fig. 1. (A) An SEM (Philips XL30FEG) image of fracture surface of aragonitic portion of abalone nacre showing aragonite (CaCO<sub>3</sub>) platelets of  $\sim$ 0.5 µm thick. (B) A TEM (Philips CM200) image of the nacre cross section revealing a <10 nm thin organic film (marked "O") between the aragonite platelets with their **c**-axis normal to the organic template.

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