logged stand of trees.
21. Litterfall data, from (9), indicate that litterfall inputs of carbon are between about 50 and 120 g m^{-2} $year^{-1}$ for coniferous forests of the Sierra transect above 1200 m elevation. We estimated carbon productivity for grasses at the Fallbrook site by assuming that their values are similar to those for other grassland soils in California (between 50 and 100 g m^{-2} $year^{-1}$ [R. Valentini *et al.*, *Ecology* **76**, 1940 (1995)].
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26. The estimates of carbon change in Fig. 3 ignore important factors, such as probable changes in carbon inputs to the soil by plants and feedbacks between SOM decomposition and plant productivity. In addition, the climate transects studied in Hawaii and the Sierra Nevada integrate long-term adjustment of ecosystems to average climatic conditions, and transient responses may not be predictable from the temperature-turnover relations derived here. However, soil incubations and soil respiration measurements have shown that on short time scales, carbon fluxes from soils are strongly dependent on temperature, with Q_{10} values ranging from 2 to 5 [J. W. Raich and W. H. Schlesinger, *Tellus* **44B**, 81 (1992); D. W. Kicklighter *et al.*, *J. Geophys. Res.* **99**, 1303 (1994)] (*25*), in accord with values, derived from Fig. 2, of 3.0 to 3.8. [Q_{10} is the rate of a biological process (here, decomposition) at one temperature divided by the rate of the process at a temperature 10°C cooler.]
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Engineered Interfaces for Adherent Diamond Coatings on Large Thermal-Expansion Coefficient Mismatched Substrates

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Adhesion of thin or thick films on substrates is a critical issue in systems where the thermal-expansion coefficients of the coating and bulk material are significantly different from each other. The large mismatch of the expansion coefficients results in the generation of very high stresses in the coating that may lead to delamination, cracking, or other deleterious effects. A method to increase the adherence of diamond coatings on tungsten-carbide and stainless steel substrates is reported based on a substrate-modification process that creates a three-dimensional thermally and compositionally graded interface. Scratch and indentation tests on diamond-coated steel and tungsten-carbide samples did not exhibit film fracture at the interface and concomitant catastrophic propagation of interfacial cracks.

There has been a considerable effort in recent years to develop adherent coatings, especially in systems in which there is a large mismatch between the thermal-expansion coefficients (*1–6*). During heating or cooling, very high stresses are induced in the coating when the thermal-expansion coefficients of the films and the substrate vary significantly from each other. These stresses frequently crack or delaminate the coating from the substrate material. A number of techniques have been developed to increase adhesion strength so that coatings remain adherent even when subjected to large compressive or tensile stresses. Some of the methods used include roughening of the surface for mechanical interlocking and the use of chemically compatible interlayers having intermediate expansion coefficients (*1–4*). These methods to enhance adhesion have been successful in some material systems; however, in very large thermal-mismatched systems, cracking or debonding of the coating can still occur.

Diamond coatings on substrates like steel and tungsten-carbide (WC) with cobalt (WC–10% Co) are thermally mismatched but are expected to have applications in cutting tools and corrosion- and erosion-resistant coatings. Many techniques have been applied to improve adhesion in this case but have met with very limited success (*1*). The main problem for the deposition of diamond thin films on these materials is the large thermal stress generated during the deposition process. Besides thermal stresses, other complicating problems such as the diffusion of carbon species and the graphitization of diamond species by iron or cobalt can reduce the adhesion strength substantially.

Several methods to improve the adhesion of diamond coatings have been investigated (*1–7*). One of the most common methods to enhance adhesion is to apply interlayers having intermediate thermal-expansion coefficients. The interlayers are expected to decrease the effect of interfacial stresses and reduce the graphitization and diffusion of carbon species during deposition. However, these methods have been only partially successful chiefly because the residual stresses are still high enough to debond from the intermediate film.

We have observed that creation of a three-dimensional (3D) thermally and compositionally graded interface between diamond and the substrate material leads to improved adhesion of the diamond film (*8*). A schematic diagram of the nature of the film in sharp and 3D chemically and thermally graded interfaces is shown in Fig. 1. The diamond film was subjected to biaxial compression while the metallic substrate was under tension. Figure 1A shows an idealized representation of the normal stresses across the cross section of the homogeneous coating and freestanding substrate at a point far from the edge. The stress distribution in the film is determined by the requirements that the normal forces, and the bending moments, over the total cross section should be zero (*9*). From the first requirement, stresses of opposite sign must form in the substrate to balance those in the film. Thus, the stress reverses sign at the interface. Because of the much larger thickness of the substrate, the magnitudes of the stresses are much lower in the substrate than in the film. The second require-

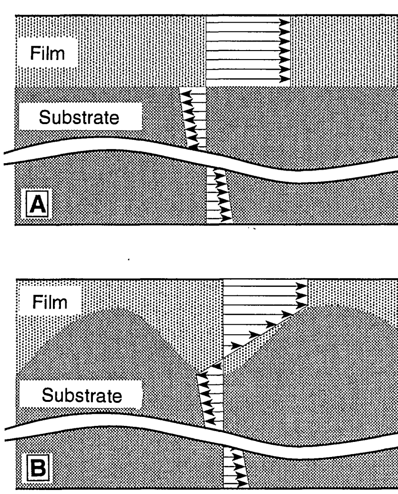

Fig. 1. Schematic diagram showing the nature of stresses present for (**A**) a planar interface and (**B**) a 3D thermally and compositionally graded interface.

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ment means that the substrate must bend to balance the bending moments produced by the stresses of the film on one of its surfaces. As the film thickness is expected to be much smaller than the substrate thickness, substrate bending is negligible. It should be noted that the delamination of the diamond film takes place usually as a predominantly shearing mode of interfacial failure.

This 3D type of interface has several advantages, especially in cases when the coating is under compressive stress. Although the overall stresses in the film do not change, the stress distribution to the interface is much different from that for the sharp, well-defined interface. In this case, the stresses at the graded interface are expected to be lower. One important feature of this 3D interface is that the interface is not parallel to the surface but inclined at an angle from 30° to 80° from the direction of the maximum compressive stresses. In addition, the high degree of compressive stresses provides a means to interlock to the substrate mechanically. Also, higher adhesion strength is expected from the larger interfacial area created by this method. Thus, the creation of a 3D interface is expected to increase the adherence strength of the coating substantially.

To create the 3D interface we have developed a multiple-pulse laser irradiation technique. The details of the technique to create this surface have been discussed elsewhere (*8*). Briefly, multiple nanosecond laser pulses with energy densities near the ablation threshold are used to create a microrough surface morphology (*10*). The periodicity and the roughness of the laser-induced microrough structures (LIMS) depend on the input laser parameters. Experiments have shown that the primary mechanism for formation of LIMS is the spatially nonuniform etching of the surface. Under certain irradiation conditions, specific areas on the surface, like grain boundaries, act as preferential etching sites, leading to the formation of LIMS.

Once the microrough structures were formed on the surface of WC–10% Co and 418-steel, diamond films were deposited by two techniques: hot-filament (HF) chemical vapor deposition (CVD) and electron cyclotron resonance (ECR)–assisted CVD (*11–13*). Standard deposition conditions were used for both methods. One important difference between the two techniques is the substrate temperature used for the process. In the HF-CVD method, the substrate temperature was ~900°C, whereas the substrate temperature in the ECR-CVD system was between 500° and 550°C. Reduced temperature was essential for fabricating adherent diamond films on steel substrates. In the case of the WC–10% Co substrates, the substrates were etched with HCl solution to remove the surface cobalt, which would have induced graphitization of diamond.

The surface morphology of WC–10% Co after the laser surface-modification process is shown in Fig. 2A. To depict the roughness on the sample, we obtained the image at a 60° tilt from the surface. Microrough structures formed after the laser irradiation process. This surface was created with 600 laser pulses having energy densities in the range of 3.0 to 6.0 J/cm^2. The average roughness was 10 μm with a feature periodicity of ~20 μm. The surface morphology of a diamond film deposited on a WC substrate at two different magnifications is shown in Fig. 2, B and C. The films were deposited by the HF-CVD technique under standard deposition conditions. On the basis of thermal stress consideration only, a compressive stress of 2 GPa is expected in the film. Continuous diamond films (~5 μm thick) formed at the surface of the material. Because of the surface modification process, the diamond exhibits large-scale periodic surface roughness. However, the inherent surface roughness of the film is much less than that of the starting material. No delamination or cracking of the film was observed. Raman measurements done on this film confirmed the diamond phase along with small amounts of graphitic impurities.

To examine the adhesion of the diamond films on WC substrates, we conducted both scratch and indentation tests on these samples (*14, 15*). Indentation tests were performed with a Rockwell hardness tester in which the diamond-coated sample was indented with different loads (60 to 150 kg). Qualitatively, for films of equal thickness, the minimum loads at which the coating fracture occurs (P_{cr}) by indentation can be used as a relative measure of coating adhesion. When fracture occurs, a lateral crack is initiated and propagates along the substrate-film interface, leading to debond-

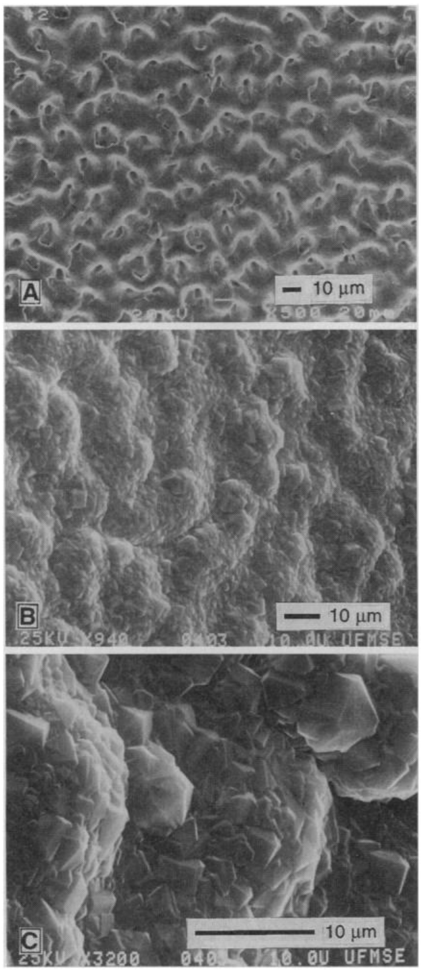

Fig. 2. Micrographs of (**A**) a surface-modified WC–10% Co surface and diamond film deposited on this surface at (**B**) low and (**C**) high magnification.

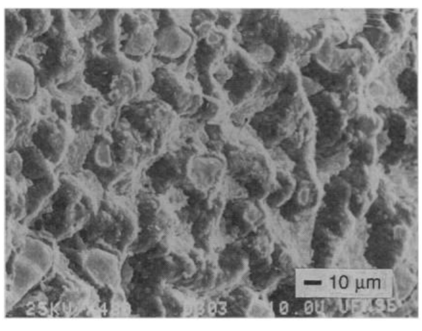

Fig. 3. The surface of diamond-coated WC–10% Co after diamond scribing. Note that the tips of the substrate have been broken without any fracture in the film.

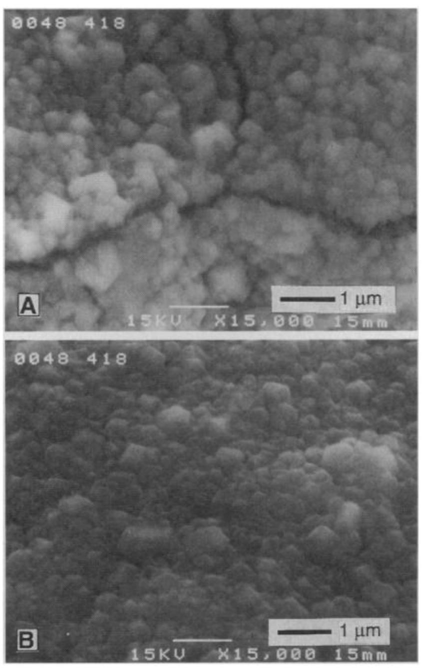

Fig. 4. Scanning electron micrograph of diamond films deposited on (**A**) planar and (**B**) surface-modified TiN-coated 418-steel substrates.

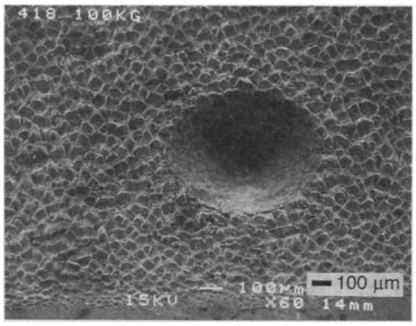

Fig. 5. Rockwell indentation tests conducted on diamond films on a TiN-coated 418-steel substrate that had been morphologically surface modified.

ing of the coating. The diamond film on WC–10% Co substrates did not exhibit any signs of visible delamination for indentation loads of up to 150 kg, thus qualitatively confirming excellent adhesion of the film.

Qualitative scratch tests were also conducted on these samples. In these tests, the coating adhesion is related to the minimum load at which stripping of the diamond film occurs. The stripping of the diamond film is attributed to film fracture, which results in propagation of the crack along the interface. In our scratch tests, no catastrophic failure of the film at the interface was observed. However, the substrate was found to deform and fracture before failure of the diamond film at the interface (Fig. 3). The film thickness was ~5 µm, so complete filling of valley features was not achieved. The tip regions of the microrough bulk materials were removed by the scratch tests. However, no catastrophic failure of the diamond film was observed. No cracks or visible marks of delamination were observed in the diamond film, attesting to the good adherence of the film.

The surface modification method also was found to increase the adhesion of diamond films on type 418-steel substrates substantially. Steel remains an elusive substrate for the deposition of adherent diamond thin-films. Besides large thermal stresses, graphitization of depositing carbon species and rapid diffusion of carbon into the steel substrates prevents growth of diamond films. To overcome some of these barriers, we adopted a three-step process. First, LIMS were created on the stainless steel surface. For steel, the samples were processed in a vacuum to reduce the shock wave–related effects that can limit the formation of microrough structures. LIMS in steel have a periodicity and roughness of ~100 µm. After the creation of the LIMS, the surface was coated with a TiN diffusion barrier that prevents graphitization and diffusion of carbon species. Finally, the diamond films were deposited on these substrates with the ECR-CVD technique at temperatures in the range of 525° to 550°C. To compare the effectiveness of the surface roughness, we also deposited diamond films on unmodified TiN-coated 418-steel substrates. The surface morphology of the diamond films deposited on laser-modified and smooth surfaces is shown in Fig. 4. Although the surface morphology of the diamond film in both samples was approximately the same, diamond films deposited on the unmodified steel showed substantial cracking and debonding.

The adhesion of the diamond film on the steel substrate was quantified by Rockwell indentation tests conducted with a brale indenter. Figure 5 shows a micrograph of indentation tests conducted on diamond samples deposited on a laser-modified surface. Partial delamination of the film was already observed in the diamond film deposited on unmodified TiN-coated steel substrates (Fig. 4A). Although the microrough steel substrate plastically deforms with the application of the load, the diamond film did not catastrophically fracture even when a load of 150 kg was applied by the indenter. The surface roughness of diamond can be minimized by controlling film nucleation. Thus, this method shows immense promise for the fabrication of adherent coatings in large thermal-expansion mismatched systems.

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A Role for Brassinosteroids in Light-Dependent Development of *Arabidopsis*

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Although steroid hormones are important for animal development, the physiological role of plant steroids is unknown. The *Arabidopsis DET2* gene encodes a protein that shares significant sequence identity with mammalian steroid 5α-reductases. A mutation of glutamate 204, which is absolutely required for the activity of human steroid reductase, abolishes the in vivo activity of DET2 and leads to defects in light-regulated development that can be ameliorated by application of a plant steroid, brassinolide. Thus, *DET2* may encode a reductase in the brassinolide biosynthetic pathway, and brassinosteroids may constitute a distinct class of phytohormones with an important role in light-regulated development of higher plants.

Plant growth and development are governed by complex interactions between environmental signals and internal factors. Light regulates many developmental processes throughout the plant life cycle, from seed germination to floral induction (*1*), and causes profound morphological changes in young seedlings. In the presence of light, hypocotyl growth is inhibited, cotyledons expand, leaves develop, chloroplasts differentiate, chlorophylls are produced, and many light-inducible genes are coordinately expressed. It has been suggested that plant hormones, which affect the division, elongation, and differentiation of cells, are directly involved in the response of plants to light signals (*2*, *3*). However, the interactions between photo-

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