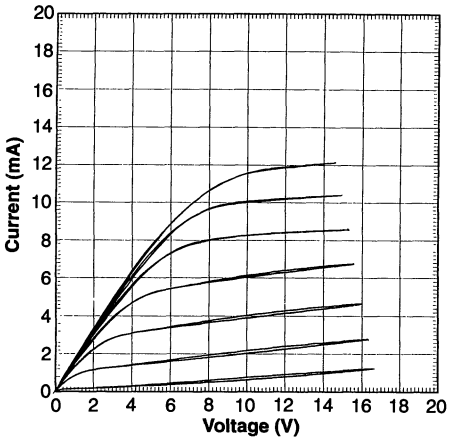

Fig. 4. The drain-to-source current (I_{DS}) as a function of the drain-to-source voltage (V_{DS}) at different gate biases (V_g, 1 V per step) for a typical GaS-GaAs FET.

≤1.6 pF, consistent with 300 Å GaS with a relative dielectric constant of 11.

The molecular design of a cubic phase of GaS allows for the fabrication of a new class of GaAs transistor, what we term a FET with an insulating sulfide heterojunction. This device is in the general class of a MISFET and represents the first step toward the realization of a III-V analog to the commercial silicon MOSFET device. These GaS-GaAs devices have isolation between the gate circuit and the source-drain circuit superior to that of GaAs MESFETs of comparable geometry. In contrast, the lack of any insulator between the gate and the channel in MESFETs results in large current conduction through the gate electrode. In addition, the GaS-GaAs FETs show better on-off switching properties, as measured by the resistance ratio, than MESFETs under comparable operation conditions. Our experimental data demonstrate that, even without optimization, the cubic phase of GaS can be used to construct a GaAs MISFET with good transconductance and input-to-output isolation and acceptable dc characteristics. A further advantage of cubic GaS lies in its method of growth, MOCVD, the accepted method of growth of GaAs-based devices. Thus, the ability to grow a gate insulator layer by the same methodology is a distinct advantage of cubic GaS as a potentially viable material for the enablement of GaAs digital devices. This cubic GaS insulating phase should make it possible to design new types of III-V–based devices.

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Diamond Coating of Titanium Alloys

M. D. Drory and J. W. Hutchinson

A titanium alloy was coated with a thin layer of synthetic diamond by chemical vapor deposition methods, achieving exceptional adhesion. Scientific and technological opportunities exist for the development of diamond-coated metal alloys and for a better understanding of adhesion mechanisms of hard, brittle coatings. An indentation method of wide applicability for measuring the adhesion of such coatings is discussed.

There has been considerable effort in recent years in the development of bonding technologies for metal and ceramic materials to produce strong interfaces of known mechanical reliability with a major emphasis on obtaining quantitative measures of adhesion (*1*). These efforts have necessarily crossed several science and engineering disciplines, including chemistry, materials science, and mechanics. Such attention arises from the increased use of metals with ceramics in high-technology applications from turbine engines to microelectronics. For example, advanced electronic packaging involves numerous metal-ceramic couples for device attachment and interconnections with chip carriers (*2*). In this application, thin metal films are deposited on a ceramic substrate. Problems in reliability may arise with ceramic packaging as with other metal-ceramic bonds because of materials processing or temperature changes in fabrication and use (such as heat generated by an electronic device). The large residual stresses that result may cause failure of the interface, substrate, or film. Specifically for the thermally induced stresses in a film or coating, σ_{th}, the magnitude scales with differences in the coefficient of thermal expansion, $\Delta\alpha$, and with temperature change measured from the stress-free state (usually the processing temperature), ΔT, by

$$\sigma_{th} \approx E\Delta\alpha\Delta T \quad (1)$$

where E is the film's Young's modulus.

These issues of reliability associated with metal-ceramic systems are greatly exacerbated for the related problem of synthetic diamond thin films deposited on metal substrates. In this case, enormous residual (thermal) stresses arise from large thermal expansion differences ($\Delta\alpha \sim 5 \rightarrow 10 \times 10^{-6}$ K^{-1}) and from an extreme value of the Young's modulus of diamond ($E \sim 1000$ GPa). The magnitude of the stress can be expected in this system of materials to exceed several gigapascals of compression.

Despite the large stresses expected for diamond-coated metals, a thin diamond layer is usually sought for many applications because of its extreme hardness, stiffness, thermal conductivity (at room tempera-

M. D. Drory, Crystallume, Menlo Park, CA 94025, USA. J. W. Hutchinson, Division of Applied Sciences, Harvard University, Cambridge, MA 02138, USA.

ture), and corrosion resistance. In particular, development of diamond-coated steel is considered an important goal in synthetic diamond technology because of the profound commercial importance of enhancing the abrasion resistance of commercial alloys (such as surgical knives and bearings). Current efforts are focused on coating steel and other metal alloys with diamond produced by chemical vapor deposition (CVD) methods. [Details of the CVD diamond process are discussed elsewhere (3).]

In addition to a large thermal expansion mismatch, the diamond-coating of steel is made difficult by the chemical incompatibility between steel substrates and the CVD deposition process. In particular, carbon solubility and adverse reactions with alloying elements necessitate the use of an interlayer, for providing a diffusion barrier, or the use of diamond-like carbon (DLC) (4). However, these approaches are prone to poor coating adhesion and a consequent reduction of the desired physical properties for many applications (such as hardness and thermal conductivity). The focus of our work here is to describe our initial efforts in diamond-coating metals and our attainment of exceptional interface adhesion. An important ancillary issue is quantifying the adhesion properties of diamond-coated metals, a particularly difficult task because of the extreme hardness and stiffness of diamond (5).

We explored diamond-coating of metal alloys using as a substrate a commercial titanium alloy of Ti-6Al-4V that is widely used in aerospace applications. This substrate material permits exploration of the deposition and adhesion measurement issues for diamond-metal couples with a large thermal expansion mismatch but without the complications associated with adverse chemical reactions at the interface. We prepared coupons of Ti-6Al-4V (25 mm by 5 mm by 1 mm) for diamond deposition by cleaning them in solvents (acetone and 1,1,1-tricholorethane). The samples were lightly abraded with a fine diamond powder for nucleation enhancement and rinsed in deionized water. Diamond growth was achieved in a microwave plasma reactor at an excitation of 2.45 GHz in a hydrogen gas mixture with ~1% methane at a sample temperature of ~800°C. The total gas flow rate was 200 to 250 standard cm^3 min^{-1} at a pressure of 30 to 80 torr.

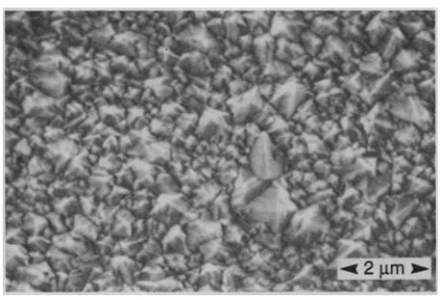

Fig. 1. Scanning electron micrograph revealing the microstructure of the diamond coating on the titanium alloy.

The titanium coupons were then coated with a thin diamond layer ~1 μm thick. Evidence of diamond growth was confirmed by a characteristic peak on the Raman spectrum and a fine-grained and well-faceted microstructure (Fig. 1). A pronounced shift in the Raman spectrum from 1332 cm^{-1} to 1350 cm^{-1} (relative wave numbers) was analyzed (6) and indicates that an enormous (compressive) stress of ~7 GPa is maintained in the film at room temperature after deposition. This contrasts with previous attempts at diamond-coating titanium, where delamination was reported (7).

The successful coating of a titanium alloy is important because of the practical importance of titanium as an alloy and indicates as well the use of titanium as a potential metal interlayer for the coating of other metals. However, the very large interface adhesion achieved with the diamond-titanium system also presents a considerable challenge for quantifying the adhesion with a test that measures the interface fracture toughness, G_c. This quantity represents the energy per unit area needed to drive a delamination crack along the interface. Delamination of films under high compression usually takes place as a predominantly shearing mode of interface failure, with crack faces remaining in nominal contact, as opposed to a tensile opening mode of fracture. This type of failure is designated as mode II cracking in fracture mechanics terminology and, for interface delamination, tends to be linked with high toughness.

Measurement of the interface toughness for a diamond-coated substrate is complicated by many of the physical properties that make diamond an attractive material for abrasive resistance applications: namely, extreme values for hardness (80 to 100 GPa) and for the Young's modulus (1000 GPa) (8). As a result, nearly all current adhesion testing methods are of limited value. For example, a common method of testing coating adhesion involves scribing the coated surface with a diamond-tip indenter under increasing load until delamination is observed. In some cases, the failure load may be related to interface toughness. However, for very hard films tip erosion during scribing greatly complicates the interpretation of the delamination load (9).

Another method for measuring the interface toughness relies on inducing a delamination region by penetration of the coating with a pyramidal (Vickers) diamond indenter (10). This test has been applied to measure the interface toughness of ZnS on glass substrates. Delamination is induced by plastic flow of the film; hence, a relatively low yield (flow) stress compared with that of the diamond penetrator is required. This technique leads to indenter failure because of the extreme hardness of the diamond film when it is deposited on a brittle substrate (11). An important exception is the indentation of diamond films on relatively ductile substrates, and this method is described below for the specific example of measuring the interface toughness of diamond-coated titanium substrates. Separate analyses are needed to describe the results of indentation experiments with Vickers and brale indenters.

Indentation of a diamond film may be performed on a metal substrate, inducing film delamination of radius R without indenter failure (Fig. 2). This contrasts with the Vickers indentation experiment because in this case delamination is driven by the plastic flow of the substrate rather than by the deformation of the film. The specific test geometry is shown schematically in the insert in Fig. 3, with a diamond brale indenter penetrating the film and substrate under relatively large loads (~1500 N). The cone-shaped brale indenter was used because its larger size permits a relatively large plastic zone to form in the substrate with an indentation depth that is large compared to the film thickness (t). The diamond penetrator and testing equipment are the same as used for the Rockwell hardness measurement (12), an important practical feature of this test because the Rockwell hardness measurement is a simple procedure of relatively low cost that is widely used on common industrial equipment. Testing proceeds by indenting the

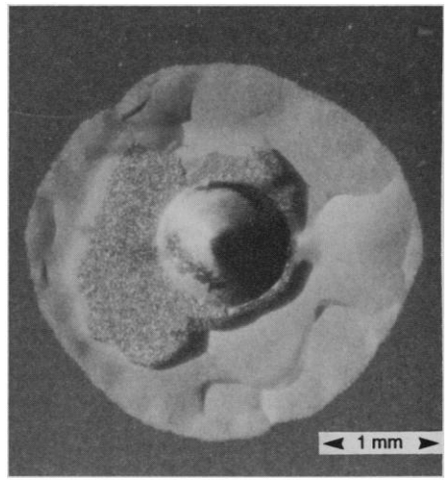

Fig. 2. Low-magnification optical micrograph of our test results.

coated surface at several locations and over a range of applied loads (~600 to 1500 N). This test has been applied to other coatings of high hardness (such as TiC or TiN); however, mechanics solutions for extracting the interface toughness, G_c, were incomplete (*13*).

Indentation of the diamond-coated titanium alloy produces several fracture events along with the interface crack (Fig. 2), such as film splitting in radial and circumferential directions. The consequences of these other fracture events on the measurement of adhesion (vis-à-vis the delamination crack of radius R) are discussed elsewhere (*5*). The dominant feature seen in Fig. 2, which enables one to obtain a good estimate of the interface toughness, is the spread of the interface crack out from the indentation to a well-defined radial distance R. A mechanics solution for the energy release rate G available to drive the interface crack as it spreads from the indent allows one to identify the value of G where the crack arrests; this is the interface toughness G_c.

The elastic strain energy per unit area stored in the film prior to indentation is $(1 - \nu)\sigma^2 t/E$, where the initial state of stress is an equibiaxial compression σ parallel to the plane of the film, ν is the Poisson ratio of the film, and t is its thickness. For values representative of the diamond-titanium system (σ = 7 GPa, t = 1 μm, ν = 0.07, and E = 1000 GPa), the initial strain energy per unit area is 46 J m^{-2}. Although delamination may be accompanied by a number of other failure mechanisms (film splitting and buckling), our discussion focuses on the dominant fracture event involving an axisymmetric edge delamination of radius R (Figs. 2 and 3). The indenter plastically deforms the substrate, forcing the metal to pile up and expand radially. The indentation radius a is very large compared to the film thickness, with the important consequence that the bending energy induced in the film is very small compared to the change in the strain energy brought about by the in-plane deformation of the film. Assuming the film remains attached, it must undergo the same in-plane deformation as the substrate surface, resulting in an increase in the in-plane radial compressive stress σ_r in the vicinity of the indenter.

A recent numerical solution to the conical indentation problem (*14*) provides the radial distribution of the radial component of stress σ_r in the attached film as a combination of the initial stress and that of the indenter. This, in turn, permits the determination of the energy release rate available to drive an edge delamination with the crack tip at radius R. For a delamination with a relatively narrow annular strip of intact film trailing the tip (*15*), the value for G is

$$\frac{(1 - \nu^2)\sigma_r^2 t}{2E} \qquad (2)$$

Curves of G/G_0 as a function of R/a are shown in Fig. 3 for the ratio of various levels of initial stress to the Young's modulus (σ/E). The value G_0 used in the normalization is the energy release rate available before indentation that is attributable to the residual stress alone (if a free edge is introduced). It is given by Eq. 2, with σ in place of σ_r, and has the value 24 J m^{-2}, which is based on the values cited above. The stress level induced in the film within about one indenter radius from the edge of the indenter is very high, and the energy release rate in this region is many times the value for G_0; for larger values of R/a, G gradually falls to G_0. For our diamond-titanium system, the delamination crack is observed to spread until R/a is ~2.5. From the curve for σ/E = 0.007 (Fig. 3), it can be seen that G/G_0 is ~1.8, giving a value of G_c of ~44 J m^{-2} for the toughness of our diamond-titanium interface. This toughness value is representative of a reasonably strong metal-ceramic interface and is at least an order of magnitude higher than that for brittle interfaces.

The interface toughness of the diamond-titanium system is considerably greater than the adhesion properties of many other diamond-coated materials. Usually, delamination occurs on cooling from the diamond deposition temperature on most metal and ceramic substrates even though the residual stress is considerably less than that of the present system. This indicates that the diamond-titanium system permits the examination of the role of interface chemistry and surface roughness on the adhesion properties of highly stressed films. In particular, an interface reaction layer may be present to promote chemical bonding while the surface roughness may play a role in the mechanical interlocking of the film and substrate. These are among other mechanisms that are believed to interact synergistically for the attainment of great interface toughness on dissimilar materials (*16*). The diamond-titanium system provides an opportunity to explore these effects on an adherent film under large residual compression.

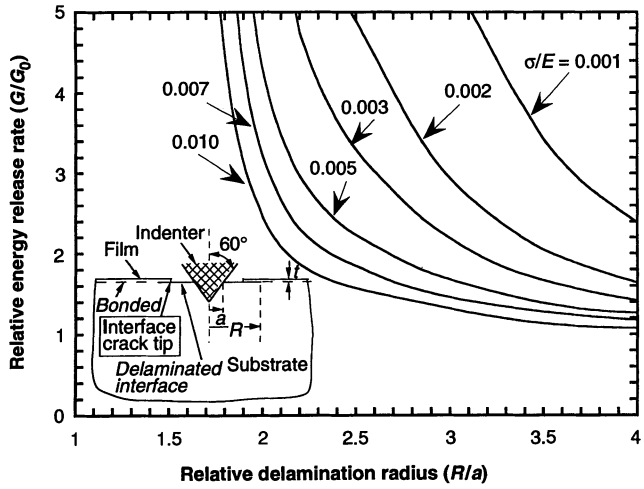

Fig. 3. Trends in the energy release rate with changes in the delamination radius and a schematic of the adhesion test with a diamond indenter (inset).

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