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On the mechanical integrity ratio of diamond coatings

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Abstract

A new concept is introduced for the quantitative measurement of the protection afforded to the substrate by a given coating — i.e., the mechanical integrity ratio. This measurement is based on the soft impressor technique and is demonstrated with particular reference to diamond coated:silicon (001) substrate surfaces. In particular, the integrity ratio has been measured for specimens coated with a hot-filament CVD process, using different concentrations of methane in hydrogen during growth and also for specimens of different thickness grown under fixed growth conditions (1% methane). In this work, various types of failure of the coated system are identified and the method is used to demonstrate how the maximum thickness of coating may be determined — i.e., that above which no further protection is to be gained. © 1997 Elsevier Science S.A.

Keywords: Mechanical integrity ratio; Diamond coatings; Quantitative measurement; Protection

1. Introduction

The lack of a reliable and quantitative method of measuring the mechanical integrity of a coated system is widely acknowledged [1–3]. Diamond coatings present the ultimate challenge in this respect since most of the available indirect methods are based on deforming the surface with a hard rigid stylus or indenter, and accuracy in the nature and geometry of the resultant point contact can be neither predicted nor controlled.

Here, a new approach to this problem is introduced — i.e., the use of the soft impressor method to measure the mechanical integrity ratio (I_R). It is anticipated that this measurement will be of interest to those responsible for the development of coating processes and to the design engineer who is required to select coatings capable of affording a guaranteed level of protection to a given substrate material. Furthermore, this investigation represents the first opportunity to demonstrate the potential of the soft impressor technique, using specimens which have been produced under controlled and well-characterised growth conditions, with results which can be published without the constraints of commercial confidentiality.

Intrinsically, the method is applicable to all coated systems but here we have concentrated upon the protection given by coatings to (001) silicon substrates.

2. Experimental

2.1. Growth conditions and structure

The coatings were all grown on a (001) surface of single crystal silicon which had been manually abraded with 1–3-μm diamond powder prior to deposition. They were produced by a standard hot-filament chemical vapour deposition method [4]. Briefly, the basic conditions were: substrate temperature ~900°C; tantalum filament temperature ~2000°C; process pressure of 20 Torr; and total gas flow of 200 sccm. These conditions gave an average deposition rate of 0.5 μm h^{-1} and the final thickness of each coating was determined by measurement in a scanning electron microscope on a section through the coated specimen. In one set of specimens, the percentage of methane was varied in the hydrogen gas mix whilst producing coatings which were 3–3.5 μm thick (see Table 1). In another set of specimens, the growth conditions were fixed, using 1% methane throughout, whilst extending the deposition time in order to provide a range of coating thickness.

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2.2. Measuring the mechanical integrity ratio

The soft impressor technique, in which conventional rigid diamond indenters are replaced by cones made from materials significantly softer than the specimens, has now been used to measure a wide range of mechanical properties [4–6]. The measured mean contact pressure (P_m), is simply the applied normal load divided by the contact area (i.e., the blunted tip of the cone), and is determined by the plastic properties of the cone material. Consequently, the magnitude of P_m can be predicted and controlled by using impressor materials of varying hardness. Other principles of the method which are particularly relevant to its use in the study of coatings include the avoidance of the type of stress concentrators normally associated with rigid indenters or sliders which may precipitate catastrophic fracture; and plastic deformation of the impressor to make intimate contact with the surface, no matter how rough it may be, whilst maintaining a uniform mean contact pressure [7]. In this latter context, the method is particularly well suited to the study of rough faceted "as-coated" surfaces.

Details of the apparatus have been published elsewhere [3] and, in these particular experiments, impressors made of silver steel or titanium diboride were used. Selective heat-treatment of the silver steel enabled a range of mean contact pressures (1.5–7.0 GPa) to be obtained.

In an earlier paper [8], we have proposed the concept of the use of the mechanical integrity ratio (I_R) to reflect the protection afforded by a coating to a specific substrate. Thus, $I_R = P'_m/P'_m$ where P'_m is the threshold mean contact pressure necessary to cause any type of failure of the coated system, whilst P'_m is that required to initiate cracks in the unprotected substrate surface. Clearly, the usefulness of this ratio will depend upon how closely experimental conditions simulate the intended application and the nature of failure will be governed both by the environmental conditions and the response of the coated system. Here, the optical transparency of the diamond coating allowed sub-surface failures to be observed directly and, since both coating and substrate tend to brittle behaviour, cracking was always the failure mode at the relevant threshold pressures.

On the unprotected silicon substrate surface, prepared ready for coating, a threshold mean pressure of 1.60 GPa (±0.5 GPa) initiated a crack on a {111} cleavage plane tangential to the area of contact with the soft impressor. On a mechanically polished (001) surface of a type Ia diamond, a threshold mean pressure of 16.4 GPa similarly caused the formation of a crack. Taking these values for P'_m and P'_m, where the latter value is assumed to represent the ultimate value for a good polycrystalline diamond coating free from significant residual stress, it appears reasonable to predict that an integrity ratio of about 10 will be the limiting value for diamond coatings on silicon substrates. It should be noted that the threshold mean pressures measured in this work develop tensile stresses in the surface, adjacent to the periphery of the contact area, which are consistent with those required to cause cleavage in these two covalent crystals [8]. In practice, it is likely that residual stress in diamond coatings on silicon substrates will limit the integrity ratio to less than 10.

2.3. Types of failure and cracking

The transparent nature of these coatings enabled direct observation of failure on the surface, the interface and the substrate material (Figs. 1–4). The various types of failure of these specimens can be summarised:

(1) Ring delamination: annular cracking developed at the coating:substrate interface where the diameter of the crack corresponds approximately with that of the circular impressor contact area. A typical example is shown in Fig. 1 caused by a mean pressure of 5.4 GPa on the specimen G 134.

(2) Complete delamination: circular cracking of the

Fig. 1. Ring delamination (1.75% Methane).

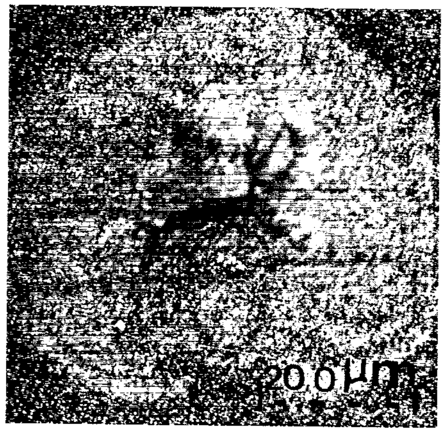

Fig. 2. Complete delamination (1.0% Methane).

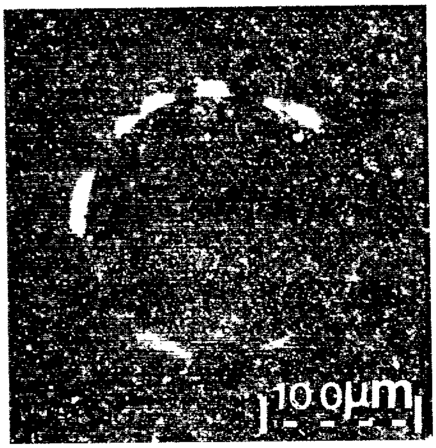

Fig. 3. Ring cracking (Coatings up to 4 µm).

Fig. 4. Partial delamination (Coatings 12–48 µm).

coating:substrate interface where the diameter may be greater, but not less, than the impressor contact area. The example shown in Fig. 2 was produced by a mean pressure of 7.1 GPa on the specimen G 130.

(3) Ring cracking: single or multiple cracks concentric with the impressor contact area and initiated in the coating by Hertzian contact stresses.

(4) Radial cracking: cracks in the coating and radiating from the centre of the impressor contact area. This type of failure was generally accompanied by complete delamination.

(5) Substrate cracking: developed in the substrate beneath the coating and generally within the impressor contact area but, in some cases, this type of fracture may take the form of ring cracks. Again, this was invariably accompanied by some other form of cracking.

3. Results and discussion

3.1. *Effect of coating structure*

The effects of methane concentration in hydrogen on the microstructure and properties of diamond coatings grown by hot-filament CVD have been reported previously [4,9]. In essence, the character of electronic bonding changes, with increasing methane content, from exclusively sp^3 to predominantly sp^2. Correspondingly, the morphology changes from highly facetted polyhedral crystallites to a less well defined, finer grained, spherical morphology — resulting in the appearance of the surface as summarised in Table 1.

Predictably, failure of the specimens studied here also depended on the concentration of methane in hydrogen during growth. Thus, with methane levels up to 1.5%, failure at the threshold pressure (P'_m) tended to be by delamination. Above this level, ring cracking was the initial type of failure observed at P'_m. At higher pressures, invariably, some degree of substrate cracking was observed irrespective of the methane concentration employed during growth. However, in this paper we limit our observations to the initial mode of failure at the threshold mean pressures and the resultant mechanical integrity ratio decreases with increasing methane concentration, as shown in Fig. 5.

Table 1

Specimen	Methane (%)	Microstructure	I_R
G133	0.5	Large microcrystals	2.6
G130	1.0	Microcrystalline	1.84
G154	1.5	Smooth nanocrystalline	1.63
G134	1.75	Medium microcrystals	1.45
G132	2.0	Very smooth, ballas/nanocrystals	1.34
G156	2.5	Very smooth, ballas/nanocrystals	1.28

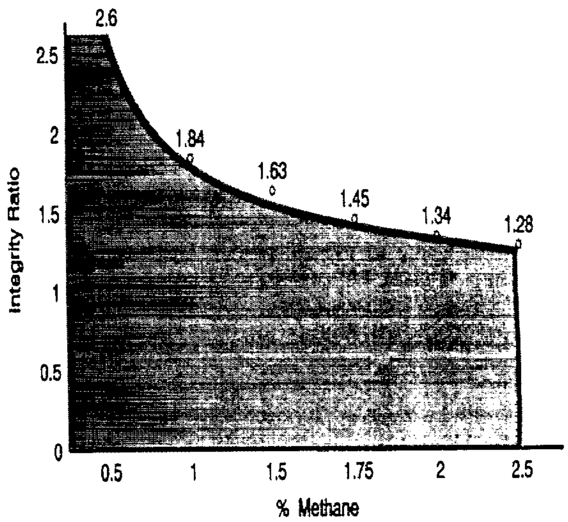

Fig. 5. Integrity ratio versus percentage of methane.

3.2. Effect of coating thickness

We have measured the threshold mean contact pressure (P'_m) to cause failure of each of six specimens of different coating thickness and the results were averaged from at least six measurements on each specimen. In Fig. 6 we have plotted the measured mechanical integrity ratio versus coating thickness on logarithmic scales. The nature of initial failure was by ring cracking in the case of coatings up to 4.0 μm thickness (Fig. 3) and by ring delamination of the interface for 12-, 22- and 48-μm coatings (Fig. 4). Full delamination of the interface was observed, directly beneath the contact area, at P'_m for the 90-μm coating, and this was followed by its complete delamination from the substrate some several hours after the measurements had been completed.

The linear relationship apparent in Fig. 6 enables us to identify three principal characteristics for this particular system under these experimental conditions. First, it identifies the minimum thickness of coating required to protect the substrate — in this case it is of the order of 1 μm. Secondly, the slope of the line can be used to estimate the efficiency of the coating in protecting the substrate. Thirdly, it is possible to determine the thickness above which the coating gives no additional protection to its substrate, i.e., about 50 μm in this case. In addition, future work may establish that the "shortfall" between the maximum value of I_R and the ultimate value of 10 is related to the residual stress in the coating.

4. Summary and conclusions

In this paper we have applied the soft impressor method to the study of diamond coated:silicon (001) single crystal substrates and have used the results to introduce the new concept of the mechanical integrity ratio — i.e., a quantitative measure of the protection given by a coating to a given substrate. The measurements have been based on two sets of specimens produced by the hot-filament CVD method: one set in which the methane concentration in hydrogen was varied in the range 0.5–2.5%; the other set consisting of coatings produced under given conditions, with 1% methane concentration, but where the deposition time was increased to give thicknesses up to 90 μm.

On the basis of our observations for the first set of specimens we may conclude that the integrity ratio decreases uniformly with increasing methane content — i.e., from 2.6 to 1.28 over the range of 0.5–2.5% methane. Also, we have observed that the nature of initial failure changes from, predominantly, delamination to ring cracking with increasing methane levels.

From the second set, we conclude that the minimum thickness to afford some protection to the substrate is about 1 μm, and that no additional protection is obtained above a thickness of about 48 μm. This corresponds to an integrity ratio of 5 compared with the ultimate value of 10 — i.e., that which might be anticipated on the basis of an ideal diamond coating — and it is suggested that the shortfall may be due to residual stress known to be present in most coatings.

Finally, the results of this study indicate that the measurement of an integrity ratio, as defined here, could be of significant assistance to those responsible for the development of specific coating processes and, more generally, to the design engineer.

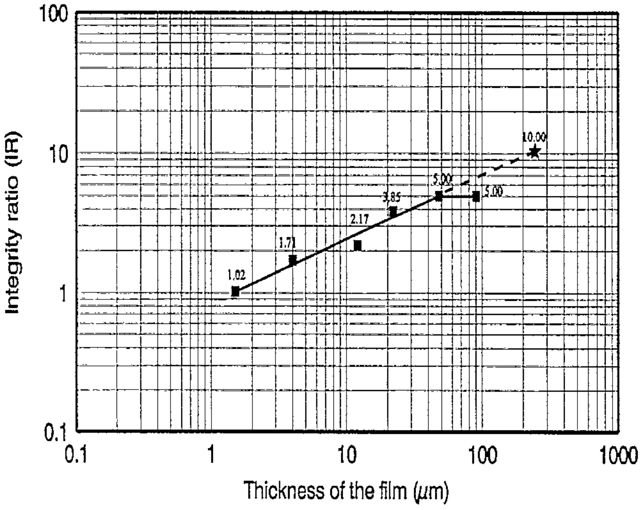

Fig. 6. Integrity ratio versus thickness of coatings.

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