

AUG 14 1988

Chemical Vapor Deposition of Diamond onto Iron Based Substrates - The Use of Barrier Layers.

P.S. Weiser and S. Praver,

School of Physics, University of Melbourne, Parkville, Victoria 3052, Australia.

When Fe is exposed to the plasma environment suitable for the chemical vapor deposition (CVD) of diamond, the surface is rapidly covered with a thick layer of graphitic soot and C swiftly diffuses into the Fe substrate. Once the soot reaches a critical thickness, diamond films nucleate and grow on top of it. However, adhesion of the film to the substrate is poor due to the lack of structural integrity of the soot layer. A thin coating of TiN on the Fe can act to prevent diffusion and soot formation. Diamond readily grows upon the TiN via an a-C interface layer, but the a-C/TiN interface is weak and delamination occurs at this interface. In order to try and improve the adhesion, the use of a high dose Ti implant was investigated to replace the TiN coating.

INTRODUCTION

Delaminated Films: We have previously reported that on Fe substrates diamond particles nucleate and grow atop the graphitic soot which initially forms on the Fe during the first few minutes of its exposure to the CVD environment [1]. Hence, in order to nucleate diamond on uncoated Fe, a sufficient thickness of graphitic soot is required to shield the incoming C species from the soot forming effects of the Fe. When Fe is coated with TiN no soot layer was observed and the diamond particles appear to nucleate and grow directly onto the TiN. These previous studies left unaddressed the nature of the Fe/TiN/Diamond interface, the Fe/Diamond interface and the quality of the adhesion between the diamond and the underlying substrate. Here we report on studies of these interfaces made possible by post deposition delamination of continuous diamond films. The back and front of delaminated films, as well as the region of the substrate from which the films had delaminated, were studied using

Scanning Electron Microscopy (SEM), Rutherford backscattering (RBS), and Secondary Electron Emission (SEE) spectroscopy.

Ti Implants: The adhesion in the Fe/diamond system may be enhanced by the formation of a TiC interface layer between the diamond film and the Fe substrate. This TiC interface may be synthesised if a buried Ti layer is formed in the steel by high dose Ti ion implantation. The success of these Ti implants as diffusion barriers was evaluated by Rutherford Backscattering Spectroscopy (RBS) and other diagnostics.

EXPERIMENT

Delaminated Films: Substrates were cut from magnet iron with dimensions $10 \times 10 \times 0.7 \text{ mm}^3$ and polished to a $\frac{1}{2} \mu\text{m}$ diamond paste finish [1]. A TiN film ($\sim 3 \mu\text{m}$) was electron-beam evaporated onto half of the substrate using a mask to shield the other half of the substrate. Prior to CVD the substrate was abraded using $3 \mu\text{m}$ diamond paste for 10 minutes and then ultrasonically rinsed in organic solvents.

The CVD diamond deposition system is described in our previous work [2]. The CVD deposition parameters were: pressure 20 Torr; Total Flow 100 sccm; $\text{CH}_4:\text{H}_2$ 1:99; temperature 1050°C ; and deposition time 12 hours.

After CVD deposition, continuous diamond films were formed on both the TiN coated and uncoated portions of the substrate. The films were found to crack and partially delaminate, presumably due to thermal mismatch. These partially delaminated films were removed from their substrate. The films were attached, with conducting silver paint, to pieces of silicon wafer for the electron spectroscopies and onto glassy carbon substrates for RBS measurements, such that the front and the back (interface) surfaces were available for analysis.

The SEE measurements were performed with a Varian Cylindrical Mirror Analyser (CMA) with a coaxial electron gun. A primary current of $0.1 \mu\text{A}$ and primary electron energy of 1 keV were used. The SEE line shapes provide clear signatures for different allotropes of carbon [3]. These signatures have been used to gain qualitative information about the nature of the bonding in the films. The RBS was performed using 3 MeV protons (H^+) and a beam diameter of $\sim 20 \mu\text{m}$.

Ti Implants: Half of the Fe substrate surface was masked and the exposed half implanted with 60 keV Ti ions using a vacuum arc technique [4]. RBS measurements showed that the retained dose was 3.0×10^{16} ions/cm². Depositions of 5 minutes and 6 hours duration were performed at temperatures of 900°C and 1000°C. The RBS measurements were performed using a focused proton (H⁺) beam (1-2 μm in radius) of 1.5 MeV which was scanned over a 150x150 μm² region of the sample.

RESULTS AND DISCUSSION

Delaminated Films: The SEM micrographs of the front and back of the films, delaminated from both the TiN coated and uncoated portions of the Fe substrate, are shown in figure 1. The microcrystalline nature of the top surface of the films is clearly evident. However, there is a noticeable difference in the films grown on TiN and Fe. The film grown on the TiN coated surface (fig. 1(a)) shows a columnar growth structure and a fairly smooth surface, whilst the film grown on uncoated Fe (fig. 1(b)) is composed of large hemispheres. This result is not surprising, given the difference between the rough amorphous soot and smooth TiN templates upon which the diamond grows in each case. The back of the film grown on the TiN (fig. 1(c)) shows a very smooth surface, which is a replica of the TiN surface upon which it was grown. However, the back of the film grown on the Fe (fig. 1(d)) is rough and resembles the previously described soot [5] which forms on the Fe.

The SEE spectra of the front and back of the films delaminated from both the TiN coated and the uncoated Fe are shown in figure 2. Using the signatures of Hoffman *et al* [6], it may be concluded from figure 2 that the surfaces of the resulting diamond film grown on the TiN (fig. 2(a)) and Fe (fig. 2(b)) are very similar; both showing the presence of diamond and some amorphous carbon. However, the back of the film from the TiN (fig. 2(c)) shows that the first few monolayers of the film are more disordered than the front of the film, with a broadening of the 15.5 and 26 eV peaks. The SEE of the back of the film delaminated from the uncoated Fe (fig. 2(d)) is once again that of graphitic soot.

Figure 3 shows the RBS spectra of the back of the film delaminated from the Fe, with a RUMP [7] simulation overlaid. The simulation was performed taking into account the non-

Rutherford nature of C and O scattering using 3 MeV H⁺. As well as the presence of the Fe, O is also present. The RUMP simulation suggests that the first 6000Å of the film contains 6.5 at. % Fe and 0.6 at. % O with an Fe diffusion tail extending up to 3½µm into the film. The Fe is possibly in the form of an oxide or carbide. The source of the Fe in the film is most likely from the soot itself. Indeed RBS measurements of the area from which the film delaminated also showed a constant 6.5 at. % Fe. This Fe acts as a source allowing slow Fe diffusion into the bulk of the diamond film, possibly along grain boundaries. By contrast, the RBS measurements of the back of the films delaminated from the TiN showed no evidence for the presence of Ti. The area of the substrate from which the film had delaminated showed no evidence for the presence of retained C.

The above results and those already published [2] combine to produce the schematic diagram of the film growth on both the TiN coated and uncoated Fe portions of the substrate shown in figure 4. The schematic diagram also illustrates the fact that not only does the TiN halt C diffusion into the Fe [1], it also halts Fe diffusing into the C, as revealed by the RBS results.

Ti Implants: The RBS spectra (1.5 MeV H⁺) from the Ti implanted and unimplanted portions of the Fe substrate after 5 minutes of exposure to the CVD deposition conditions are shown in figure 5. Both spectra show the presence of a small amount of surface O. The unimplanted portion of the sample shows that C has diffused into the Fe to a depth of 1µm. No evidence for such diffusion can be seen for the Ti implanted portions of the specimen and hence, it appears that the Ti implants are effective as diffusion barriers at 900°C (for up to 6 hours) and for 5 minutes at 1000°C. The implanted Ti cannot be observed because it is unresolved from the Fe edge. The RBS spectra from the implanted and unimplanted portions of the sample prior to exposure to the CVD plasma show no evidence for C and O.

After 6 hours of CVD at 1000°C, small diamond particles were observed (by SEM) to have formed upon a thick graphitic layer which was deposited on both the Ti implanted and unimplanted portions of the Fe sample. However, the nucleation density is greater on the unimplanted Fe. Both portions of the sample return similar RBS spectra (figure 6), showing

the formation of a thick ($>10\mu\text{m}$) C layer in which a small amount of Fe is present (up to 6.5 at. % on the unimplanted Fe). The peculiar shape of the C edge in the RBS spectrum is attributable to the surface roughness.

The above results show that the Ti implant fails as a diffusion barrier for long term exposure to the CVD plasma at 1000°C . This is probably due to the diffusion of Ti into the Fe bulk at this temperature. Once the Ti has diffused, growth on these substrates proceeds in the fashion similar to that observed for unimplanted Fe.

CONCLUSION

On uncoated Fe, a thick layer of graphitic soot containing 6.5 at. % Fe covers the substrate within the first few minutes of exposure to the plasma. Once the substrate is covered, diamond films of reasonable quality grow upon the soot. Delamination occurs within the soot layer. Some Fe diffuses into the diamond film to a depth of about $3\frac{1}{2}\mu\text{m}$. Thus, without some protective layer, it appears that it will be very difficult to deposit an adherent CVD diamond film onto Fe based substrates.

Upon TiN coated Fe, soot formation, C diffusion into the Fe bulk, and Fe diffusion into the diamond films are all inhibited. SEE spectroscopy has revealed that a thin layer of a-C lies between the TiN layer and the diamond film, and that delamination occurs at the TiN/a-C interface. Hence, whilst the problems of diffusion and soot formation have been overcome by the use of TiN barrier coatings, more work will need to be done to try to improve adhesion.

The use of a Ti implanted (3×10^{16} ions/cm²) barrier layer, in the CVD diamond deposition on Fe, is successful in halting the C diffusion into the substrate at 900°C for up to 6 hours. However, after 6 hours at 1000°C the Ti barrier layer no longer inhibits the formation of soot possibly due to the diffusion of Ti into the Fe bulk. The present results do not bode well for the use of Ti implants as C diffusion barriers for CVD diamond growth on Fe. However, other refractory metals, with lower diffusion coefficients in Fe should be investigated.

REFERENCES

- [1] P.S. Weiser, S. Prawer, A. Hoffman, R.R. Manory, P.J.K. Paterson and S-A. Stuart. *J. Appl. Phys.*, **72**(10), 15 Nov. 1992.
- [2] P.S. Weiser, S. Prawer, A. Hoffman, P.J.K. Paterson and R.R. Manory. *J. Appl. Phys.*, **76**(4), 15 Aug. 1994.
- [3] A. Hoffman, S. Prawer and M. Folman. *Appl. Phys. Lett.*, **58**(4) 28 Jan. 1991.
- [4] J.E. Galvin, B.F. Gavin and R.A. MacGill, *Review of Scientific Instruments*, **57**(6), (1986), 1069.
- [5] P.S. Weiser, S. Prawer, A. Hoffman, R.R. Manory, P.J.K. Paterson and S-A. Stuart. *Mat. Res. Soc. Symp. Proc.*, Vol. 242, 1992 MRS.
- [6] A. Hoffman, S. Prawer and R. Kalish, *Phys. Rev. B*, **45**(22), p12736, 1992.
- [7] RUMP Version 3.51 Copyright © 1985 Larry Doolittle/© 1989 Computer Graphics Service.

Figure 1 - The SEM micrographs of the front and back of the films delaminated from the TiN coated and uncoated Fe portions of the substrate. The front of the films from the TiN (a) and Fe (b) are shown above the respective back of the films from the TiN (c) and Fe (d).

Figure 2 - The SEE spectra of the front of the films delaminated from the TiN coated (a) and uncoated Fe (b) portions of the substrate in comparison to the back of the delaminated films from the TiN (c) and Fe (d) portions of the sample.

Figure 3 - The 3 MeV H⁺ ion RBS spectra from the back of the film delaminated from the Fe.

Figure 4 - A schematic diagram of the growth on both the TiN coated and uncoated Fe portions of the substrate.

Figure 5 - The RBS spectra of the Ti implanted and unimplanted regions of the sample after exposure to CVD diamond deposition at 1000°C for 5 minutes. The inset shows the detector scattering angle geometry of 170°.

Figure 6 - The RBS spectra of the Ti implanted and unimplanted regions of the sample after exposure to CVD diamond deposition at 1000°C for 6 hours.



THE UNIVERSITY OF MELBOURNE
SCHOOL OF PHYSICS

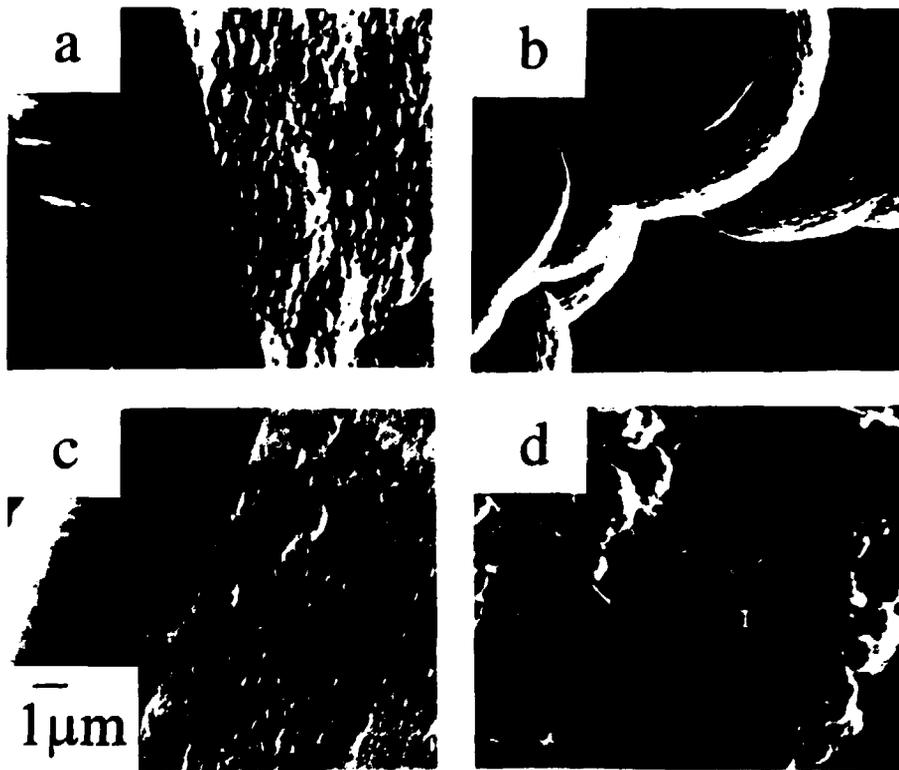


FIGURE 1.

