JOURNAL OF MATERIALS SCIENCE 26 (1991) 2441–2444

# Effects of substrate material on diamond growth from CO–$H_2$ plasma

YUKIO SAITO, KOUJI SATO, SHINPEI MATUDA
*Hitachi Research Laboratory, Hitachi Ltd, 4026 Kuji-cho, Hitachi-shi, Ibaraki, 319-12 Japan*
HIDEOMI KOINUMA
*Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 227, Japan*

Diamond synthesis from CO–$H_2$ plasma has been carried out on various substrate materials, e.g. metals: nickel, cobalt, tungsten, molybdenum, copper and ceramics: SiC, $SiO_2$, $Al_2O_3$, $ZrO_2$, AlN. Diamond formation was confirmed on every substrate with the exception of cobalt and nickel. The highest density of diamond nucleation, over $10^8$ $cm^{-2}$, was obtained on amorphous $SiO_2$, the carbide-forming metals tungsten and molybdenum and on SiC; on these the nucleation density was one order of magnitude higher than on the other substrates. Diamond films prepared on tungsten, molybdenum and SiC substrates had a strong adhesion force: 1.3 to 1.5 kg $mm^{-2}$.

## 1. Introduction

Recently, diamond has been easily synthesized by chemical vapour deposition [1], plasma-induced vapour deposition [2, 3] and ion-beam techniques [4]. In these reports, the method of diamond formation was predominantly one using a single-crystal silicon substrate.

The study of substrate material is considered to be important for the application of diamond films from the gas phase to optics, electronics and mechanics as a coating material. Spitsyn *et al.* [5] reported the dependence and variation of nucleation density of diamond grown on substrates of silicon, molybdenum, tungsten, copper and gold. Kikuchi *et al.* [6] also reported that diamond films were synthesized on metal: silicon, tantalum, niobium, tungsten, ceramic substrates: WC and SiC by ion-assisted hot-filament CVD from $CH_4$–$H_2$ mixed gas. However, the effects of the substrate material on diamond nucleation density and adhesion force of the diamond films were not discussed in detail.

Here, diamond was synthesized on various metal and metal compound substrates using the microwave plasma method with CO–$H_2$ mixed gas as previously reported [7]; the effects of substrate material on the diamond nucleation density and adhesion force of diamond films are discussed.

## 2. Experimental procedure

The experimental apparatus used in the study has been reported previously [8]. A cylindrical quartz tube reactor, 40 mm wide inner diameter and 1000 mm long was used. Various substrates such as metals: nickel, cobalt, tungsten, molybdenum, copper, metal carbide: SiC, metal oxide: amorphous $SiO_2$, crystalline $Al_2O_3$, $ZrO_2$ and the metal nitride: AlN, were used. The size of the substrate was about 8 mm wide and 8 mm long. Substrates were polished mechanically with diamond paste (mean particle size: 1 μm) for 20 min and then the polished substrates were ultrasonically washed with acetone for 1 h. Each substrate was placed on a substrate holder positioned at the centre of the reaction tube. A mixed gas composed of 10% CO and 90% $H_2$ was introduced into the tube, previously evacuated to several Pascals. A plasma was generated in the CO–$H_2$ mixed gas around the substrate by microwave radiation incident on the tube.

Reaction products on the substrate were identified by low-angle X-ray diffractometry, and the morphology of the products was observed by scanning electron microscopy (SEM). The density of diamond nucleation was determined by counting the number of sites detected in the SEM observation. The adhesion of the diamond films to the substrate was measured by a conventional pull-test.

## 3. Results and discussion

### 3.1. Observation and identification of deposits

SEM photographs and low-angle X-ray diffraction patterns of the deposits on three typical metal substrates of cobalt, tungsten and copper after 1 h reaction are shown in Figs 1 and 2, respectively. Nearly spherical deposits with diameter from 0.2 to 3 μm were observed on the cobalt substrate. X-ray diffraction peaks corresponding to graphite were detected in the deposits as well as for substrate cobalt. The reason that diamond was not formed on the cobalt substrate may be as follows: excited carbon species, necessary to

0022–2461/91 $03.00 + .12 

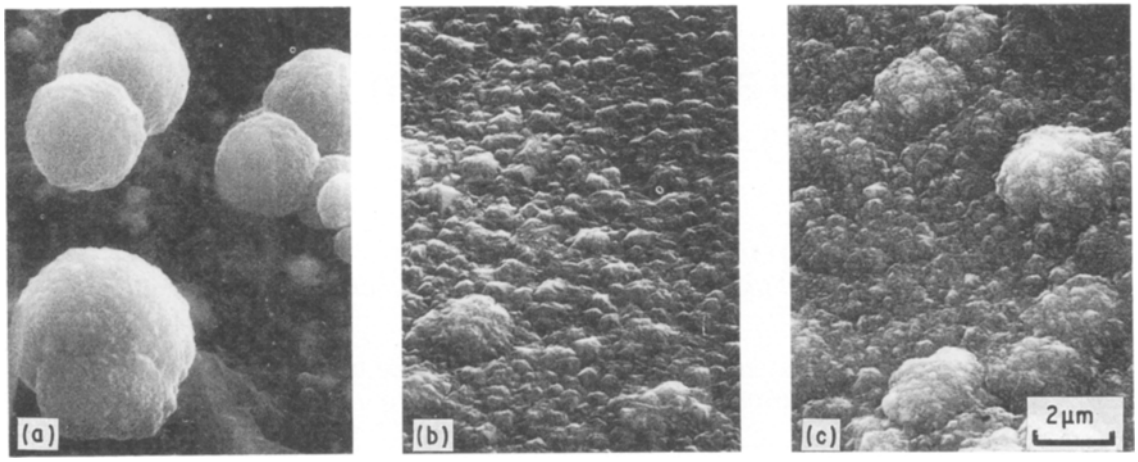


*Figure 1* SEM photographs of deposits on (a) cobalt, (b) tungsten and (c) copper substrates.

form diamond and produced in the plasma, penetrated the cobalt substrate instead to form an interstitial solid solution. A similar result was obtained also for the case of nickel. Film-like deposits with a rough surface were grown on the tungsten and copper substrates. In the case of the tungsten substrate, X-ray diffraction peaks due to WC and $W_2C$, in addition to diamond and substrate tungsten, were observed. The result suggest that initially the tungsten substrate is carbonized and then diamond crystal growth follows. Carbide ($Mo_2C$) formation was also observed on carbide-forming molybdenum. With copper, the X-ray

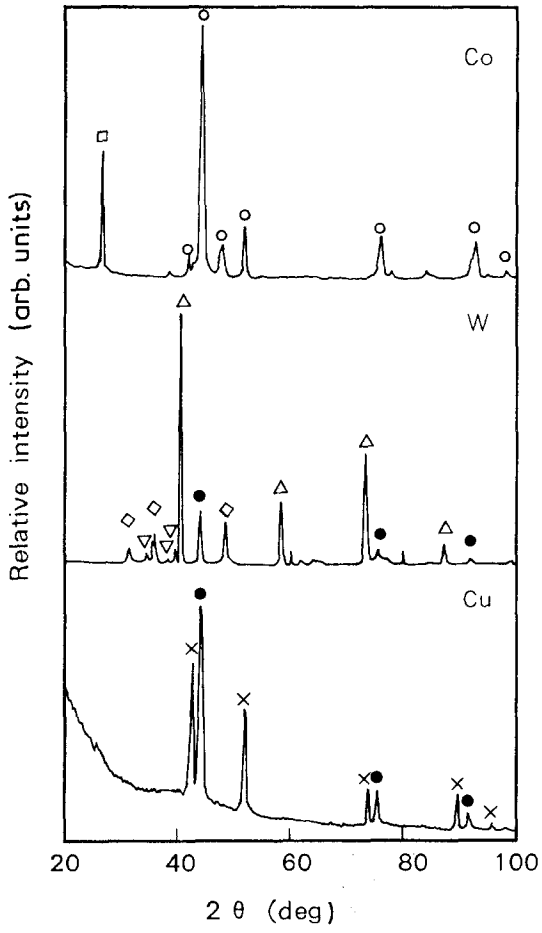


*Figure 2* X-ray diffraction patterns of deposits on cobalt, tungsten and copper substrates: (●) diamond, (○) cobalt, (□) graphite, (△) tungsten, (▽) $W_2C$, (◇) WC, ( × ) copper.

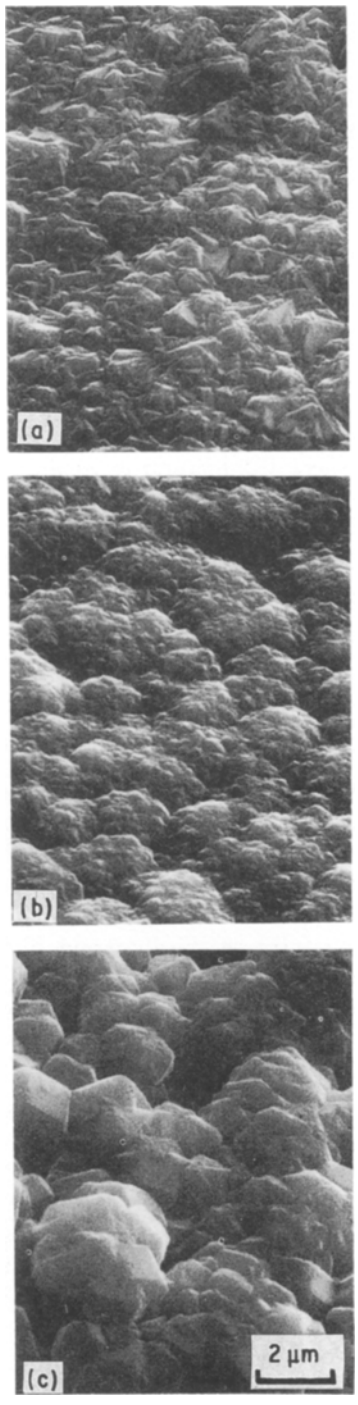


*Figure 3* SEM photographs of deposits on (a) SiC, (b) $SiO_2$ and (c) AlN substrates.

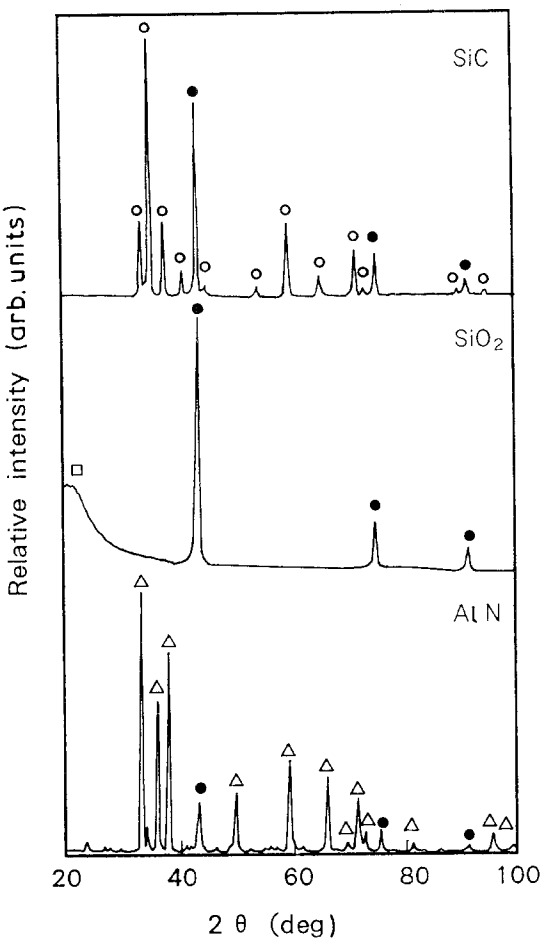


*Figure 4* X-ray diffraction patterns of deposits on SiC, $SiO_2$ and AlN substrates: (●) diamond, (○) SiC, (□) $SiO_2$ glass, (△) AlN.

diffraction pattern corresponding to diamond was obtained.

Figs 3 and 4 show SEM photographs and X-ray diffraction patterns, respectively, of deposits on the substrates of carbide (SiC), oxide ($SiO_2$) and nitride (AlN). Rough film-like deposits can be seen in all cases with little difference in morphology. X-ray diffraction patterns of these films revealed that these were all diamond.

## 3.2. Diamond nucleation density

The diamond nucleation density was determined by counting the number of diamond particles detected in unit area on a substrate by SEM. Fig. 5 shows SEM photographs of diamond nucleation and the growth process on SiC. Polishing scratches can be seen on the initial substrate. After 5 min reaction, small ball-like deposits with 0.1 to 0.2 μm size were nucleated along the scratches. Uniformity of nucleation and crystal growth were achieved after 10 min. The diamond crystal became progressively larger, and crystal coalescence was achieved after 15 min. The dependence of the nucleation density on reaction time for metal substrates is illustrated in Fig. 6. The density increases rapidly in the first stage of reaction and the nucleation rate became low after 5 min reaction. The density on the carbide-forming metals molybdenum and tungsten was about one order of magnitude higher than that on the non-carbide-forming copper. The situation for ceramic substrates is shown in Fig. 7, where a similar tend in nucleation rate was observed. The highest nucleation density, over $10^8\ cm^{-2}$, was obtained for amorphous $SiO_2$ and SiC substrates. The values for AlN and $ZrO_2$ were about $10^7\ cm^{-2}$.

## 3.3. Adhesion force

The adhesion force of diamond films to a substrate measured by conventional pull-test using epoxy resin as an adhesive agent is shown in Fig. 8. Strong adhesion forces of 1.4 to 1.5 $kg\,mm^{-2}$ were obtained

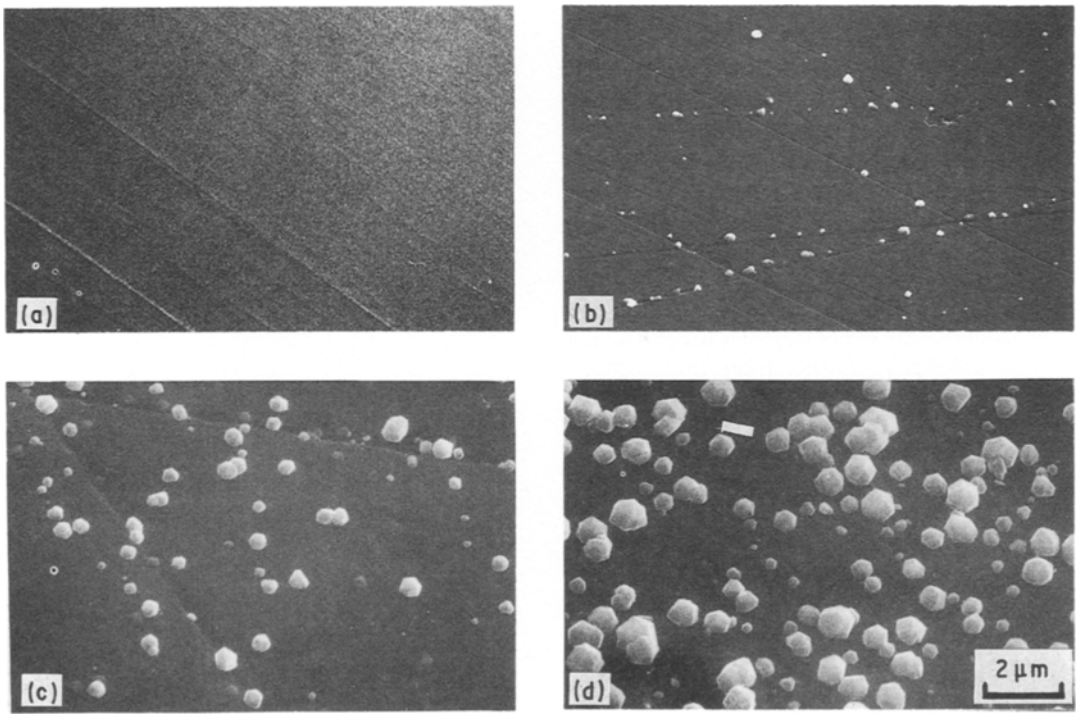


*Figure 5* SEM photographs of deposits on SiC substrate. Reaction time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min.

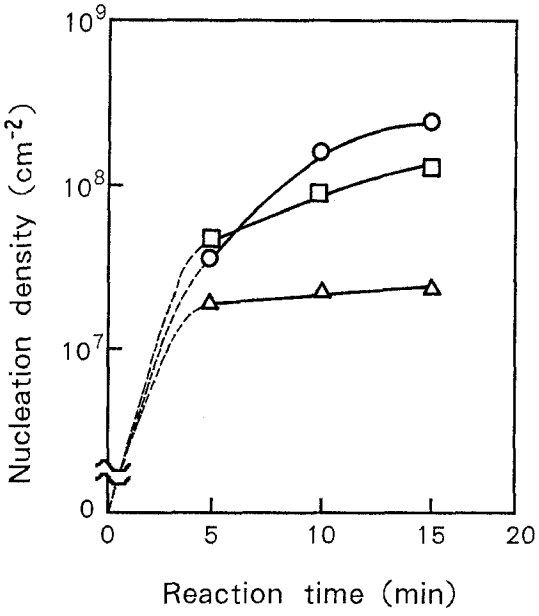


*Figure 6* Dependence of nucleation density on reaction time for metal substrates: (○) molybdenum, (□) tungsten, (△) copper.

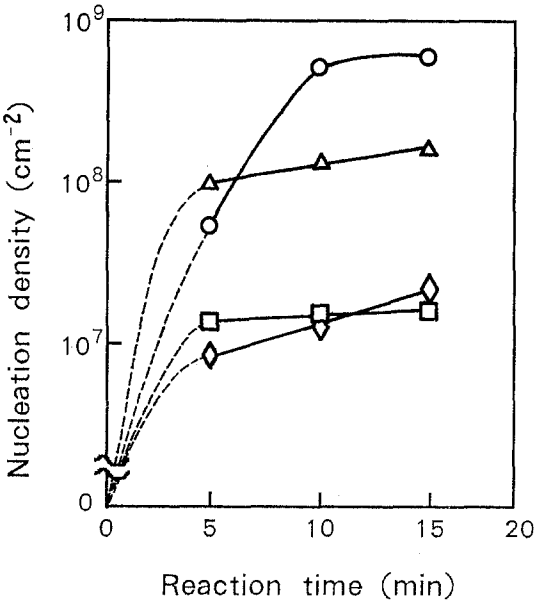


*Figure 7* Dependence of nucleation density on reaction time for non-metal substrates: (○) amorphous $SiO_2$, (△) SiC, (◇) AlN, (□) $ZrO_2$.

for the carbide-forming metals molybdenum and tungsten and for silicon carbide. These values are comparable to the adhesion force of the conventional coating films obtained by CVD or other methods. The diamond films prepared on the other non-carbide-forming metal or non-metal compounds manifested a weaker adhesion force. The diamond films formed on the amorphous $SiO_2$ substrate, which had the highest nucleation density, showed a weak adhesion force of 0.2 kg mm$^{-2}$. This result indicates that chemical affinity between diamond and the substrate is more important than nucleation density in order to get highly adherent diamond films. The strong adhesion force for carbide-forming metal or metal carbide substrates apparently originates from the penetration into the substrate of activated carbon atoms produced in the plasma.

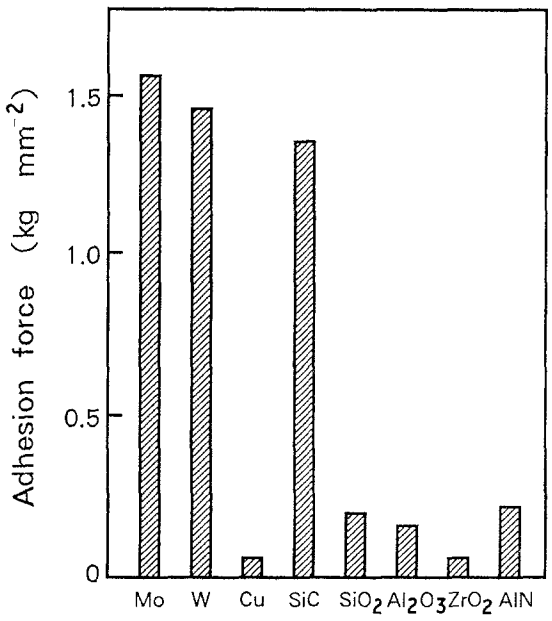


*Figure 8* Dependence of adhesion force of diamond films on type of substrate.

## 4. Conclusion

The effects of substrate materials on diamond formation were studied. Diamond crystal growth was identified on every substrate except iron-group metals, but the nucleation density and adhesion force of the diamond films varied conspicuously with the substrate material. The highest nucleation density and adhesion force were obtained in films obtained on carbide-forming metal or metal carbide substrates.


## Acknowledgements

We would like to thank Dr Kenichi Gomi and Mr Hideaki Tanaka, Hitachi Research Laboratory, Hitachi Ltd and Dr Peter E. D. Morgan, Rockwell International Science Center, California, USA for useful advice and discussions.


## References


1. S. MATSUMOTO, Y. SATO, M. TSUTSUMI and N. SETAKA, *J. Mater. Sci.* **17** (1982) 3106.
2. Y. SAITO, S. MATSUDA and S. NOGITA, *J. Mater. Sci. Lett.* **5** (1986) 565.
3. M. KAMO, Y. SATO, S. MATSUMOTO and N. SETAKA, *J. Cryst. Growth* **62** (1983) 642.
4. E. G. SPENCER, P. H. SCHMIDT, D. C. JOY and F. J. SANSALOME, *Appl. Phys. Lett.* **29** (1976) 118.
5. B. V. SPITSYN, L. L. BOUILOV and B. V. DERJAGUIN, *J. Cryst. Growth* **52** (1981) 219.
6. N. KIKUCHI and H. YOSHIMURA, *New Diamond* (Japan New Diamond Forum) **7** (1987) 26.
7. Y. SAITO, K. SATO and H. TANAKA, *J. Mater. Sci.* **24** (1989) 293.
8. Y. SAITO, K. SATO, H. TANAKA, K. FUJITA and S. MATSUDA, *ibid.* **23** (1988) 842.



*Received 20 December 1989*
*and accepted 14 August 1990*