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The effect of pretreatment in a fluidized bed upon diamond synthesis on particles by chemical vapour deposition

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Diamond synthesis was carried out on non-diamond particles (single- and poly-crystal silicon, quartz and SiC) by microwave plasma-enhanced chemical vapour deposition. Fine diamond particles were deposited on the non-diamond particle surface. The particle deposition density on the untreated particle substrates was strongly dependent on the surface characteristics of the particle substrates. The value ranged from $10–10^5$ mm^{-2} for each particle. Particle substrates were pretreated in a gas–solid fluidized bed, and these were then used for the deposition of diamond. The pretreatment of the surface of the particle substrate in the fluidized bed greatly enhanced the nucleation of diamond. A deposition density of about 10^7 mm^{-2} was obtained on single-crystal silicon particles pretreated for 15 h. The effectiveness of the fluidized bed pretreatment on the deposition density was observed to be appreciable for the four kinds of particle examined.

1. Introduction

Diamond is one of the most attractive materials because of its excellent properties, such as high hardness, good thermal conductivity and chemical inertness. Recently, diamond and diamond-like carbon have been synthesized by chemical vapour deposition (CVD) [1–4]. CVD is a useful method to synthesize fine diamond particles with uniform size, which are used as an abrasive and for the edges of cutting tools. So far, many studies have been conducted on the synthesis of diamond films on plate substrates such as silicon wafer.

It is well known that pretreatment of the substrate surface plays an important role in the nucleation of diamond. Silicon wafer substrate is often polished with fine powder [5, 6] and is sometimes pretreated with 5–60 μm diamond powder in an ultrasonic field [7]. We have investigated the pretreatment of the substrate surface using a gas–solid fluidized bed [8, 9] in which silicon wafer was immersed in the bed in which diamond, SiC or SiO_2 particles of 100–500 μm, were fluidized by gas [9]. The deposition density of diamond particles on the silicon wafer was enormously enhanced by the fluidized bed treatment and reached to about 10^8 mm^{-2}. The fluidized bed treatment could be applicable not only to such a plate but also to substrates of any shape, because the particles in the bed are fluidized in almost complete-mixing conditions.

Fine diamond particles have been deposited on plate substrates. In this case, however, a limited surface area is available for the deposition reaction. Particles as substrates are favourable for the mass production of fine diamond particles because of their large specific surface area. Only a few works have reported the deposition of diamond on particle substrates. Chauhan *et al.* [10] studied carbon deposition on 0–1 μm diamond seed crystals and reported a growth rate of 0.45 $\mu m\, d^{-1}$.

In this study, the diamond synthesis by microwave-enhanced plasma CVD was carried out on non-diamond particle substrates. Initially, the deposition density of the particles was measured and the morphology was observed when four kinds of particle were used as substrates. Next, those particle substrates were pretreated in a gas–solid fluidized bed and the effect of the fluidized bed pretreatment upon the deposition density on the particle surface was examined.

2. Experimental procedure

2.1. Samples

Four kinds of particles (single-crystal silicon (S-Si), poly-crystal silicon (P-Si), quartz (SiO_2) and silicon carbide (SiC)) were used as substrates for the deposition. S-Si particle was prepared by crushing ingots of single-crystal silicon synthesized by the Czochralski method (CZ method). P-Si particle was a commercially available one (purity 98%). The SiC particle was β-SiC. Details of the samples used in this experiment are summarized in Table I.

The particles were washed three times with acetone in an ultrasonic cleaner. SEM examination before deposition showed that there were no residual pieces larger than submicrometre on the particle surface.

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2.2. Plasma CVD

A schematic diagram of the experimental apparatus for the plasma CVD using a microwave device is shown in Fig. 1. The device was similar to that used by Kamo *et al.* [4]. Microwaves (2.45 GHz) generated by the magnetron were supplied to the quartz tube through a set of guide tubes, an isolator, a tuner and a power monitor. A plasma of reactant gas was generated by tuning a plunger and a three-stab tuner. The input power was 200 W. The position of the plasma was adjusted to the centre of the reactor. A quartz tube 30 mm i.d. and 500 mm long was used as a reactor. The particles were placed in a quartz boat which was set in the centre of the reactor. A gaseous mixture of hydrogen and methane was used as reactants, with a methane concentration of 0.5 vol %. After evacuation by a rotary vacuum pump, the reactant gases were introduced into the reactor by using two mass-flow controllers (SEC-421MARK2). The total flow rate was 500 $cm^3 min^{-1}$ at STP. The pressure in the reactor was measured using a Pirani gauge or with a mercury manometer (PB-100PC). The reaction pressure was 30 torr (1 torr = 133.322 Pa). The temperature of the particles was tentatively measured with an optical pyrometer (Pyro-Weak GMBH Hanover); it was estimated to be between 920 and 950 °C. The reaction product was examined by optical microscopy, scanning electron microscopy (SEM) and Raman spectroscopy.

TABLE I Properties of the particles

Particle	Particle diameter, d_p(μm)	minimum fluidizing velocity, U_{mf}($cm\ s^{-1}$)
S-Si	2000–4000	–
	500–1000	44
	250–500	11
	149–250	3.1
P-Si	2000–4000	–
	250–500	11
Quartz	2000–4000	–
	250–500	12
SiC	250–500	15

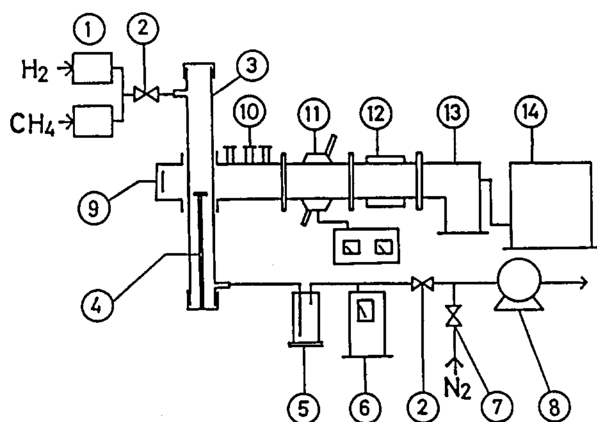


Figure 1 Schematic diagram of plasma CVD system. 1, Mass flow controller; 2, value; 3, reactor; 4, holder; 5, trap; 6, Pirani gauge; 7, leak valve; 8, vacuum pump; 9, plunger; 10, three stab tuner; 11, power monitor; 12, isolator; 13, magnetron; 14, power source.

2.3. Fluidized bed pretreatment

Fig. 2 shows the fluidized bed used for the pretreatment of the particle surface. The fluidized bed was made of acrylic acid resin, 19 mm i.d. and 445 mm long. A perforated plate was used as a gas distributor. About 2 g particles were put into the column and were fluidized by nitrogen gas at the desired gas velocity. Pretreatment was allowed to continue for 0.5–20 h.

3. Results and Discussion

3.1. Deposition on untreated particles

The deposition experiments on a single-crystal silicon particle of 2000–4000 μm were carried out. The reaction time was 1 h. Fig. 3 shows scanning electron micrographs of deposits on single-crystal silicon particles. The crystals show well-defined habits and are about the same size. Cubo-octahedral, twinned and octahedral crystals were observed. Matsumoto *et al.* [3] observed similar crystals deposited on plate substrates, while Mitsuda *et al.* [6] reported that the particles showed the clear-cut habits of cubic crystal at low concentrations of CH_4(less than 2.0%), but at a

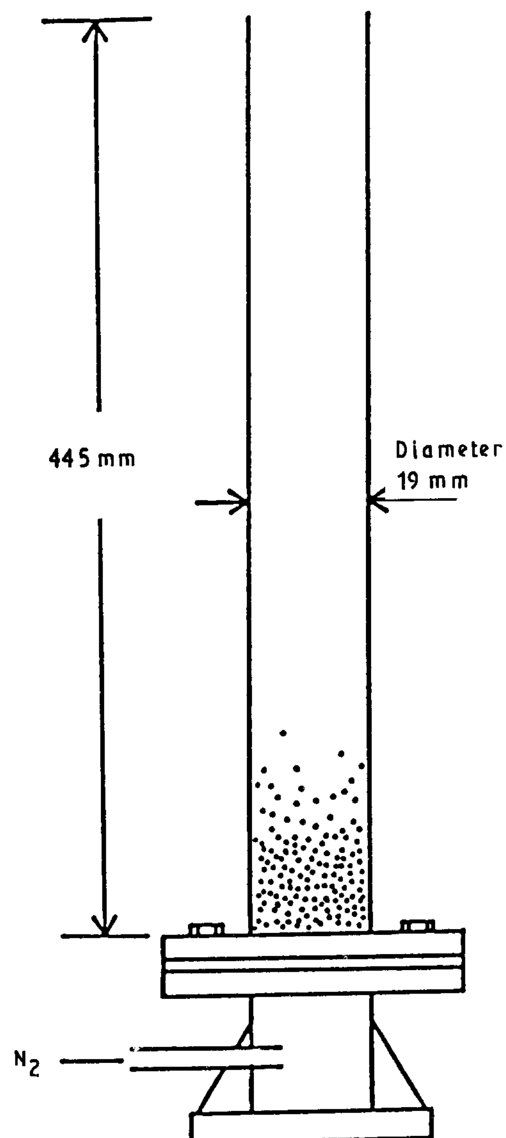
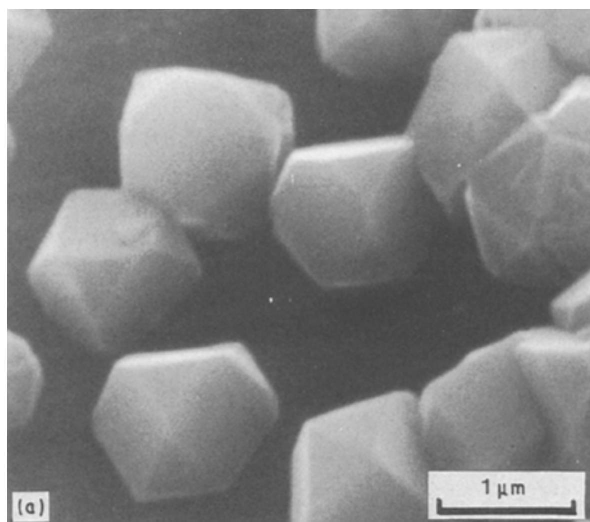


Figure 2 Schematic diagram of fluidized bed for pretreatment of particle substrates.



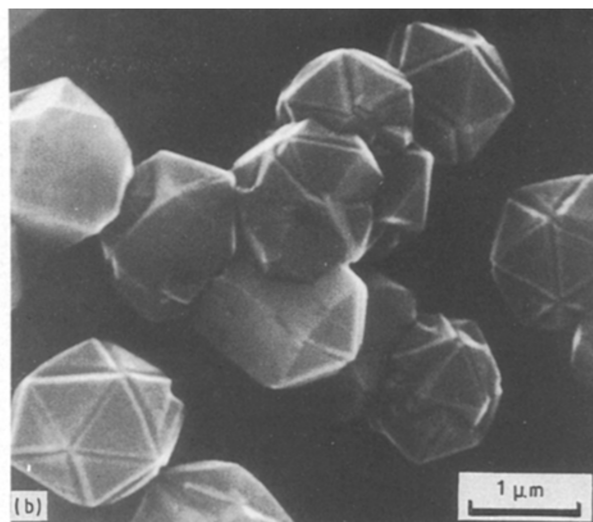


Figure 3 (a, b) SEM images of diamond particles deposited on S–Si particles. Reaction time 1 h, reaction pressure 30 torr, input power 200 W, particle substrate size 2000–4000 μm.

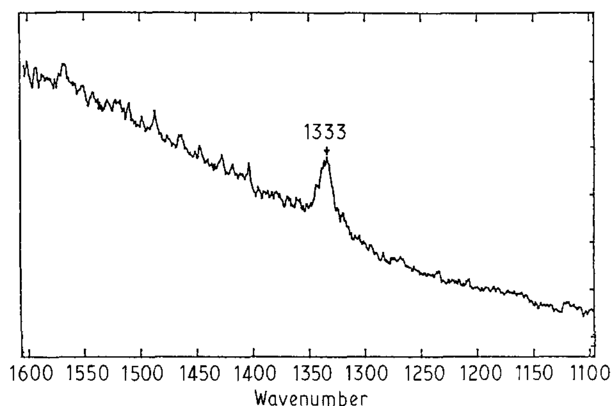
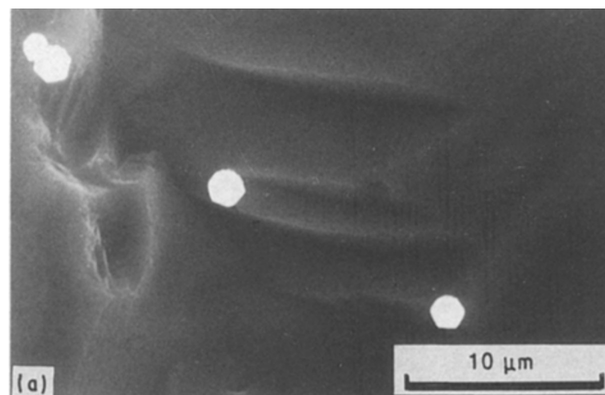


Figure 4 Raman spectrum of deposits. Particle substrate S–Si, reaction time 1 h, reaction pressure 30 torr, input power 200 W, particle substrate size 2000–4000 μm.



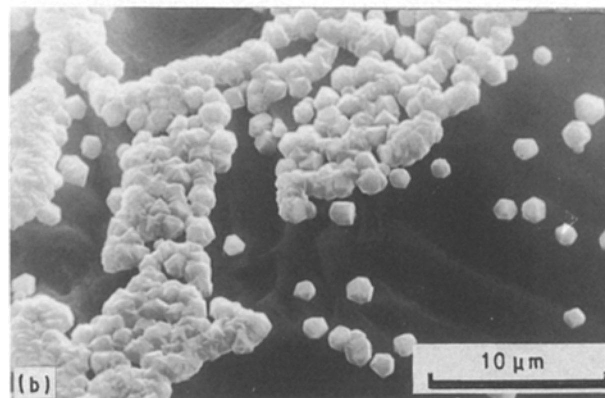


Figure 5 Typical deposition manners on the untreated S–Si particle surface. Reaction time 1 h: reaction pressure 30 torr; input power 200 W; particle substrate size 2000–4000 μm.

CH_4 concentration higher than 3.0%, spherical particles were grown. Fig. 4 shows the Micro-Raman spectrum of these specimens. A sharp peak at $1333\ cm^{-1}$ is observed. The peak at $1333\ cm^{-1}$ agrees with the reported value [11] of $1332.5\ cm^{-1}$ for the Raman line of diamond.

Six deposition runs were performed on S-Si particles under the same experimental conditions (reaction time 1 h, reaction pressure 30 torr, input power 200 W). The particle deposition density was very different for each particle. Typical deposition manners are shown in Fig. 5. The particle deposition density on some particles was quite low (Fig. 5a), while a high particle density was observed only rarely (Fig. 5b). The particle deposition densities obtained are shown in Fig. 6. The value varied widely from particle to particle and ranged from 10–$10^5\ mm^{-2}$. It is well known that when silicon wafer is used as a substrate, the deposition density on the untreated silicon wafer is quite low. We have reported [8] less than several hundred per square millimetre under similar experimental conditions to those used in this study. The deposition density obtained on some particles was appreciably higher than that for the untreated silicon wafer.

The effects of particle size, reaction time and kind of particles on the particle deposition density were examined. S-Si particles of 500–1000, 250–500 and 149–250 μm were used. The depositions on P-Si particles, quartz particles and SiC particles were also investigated. The reaction time was varied from 1–5 h. The particle deposition densities obtained are shown

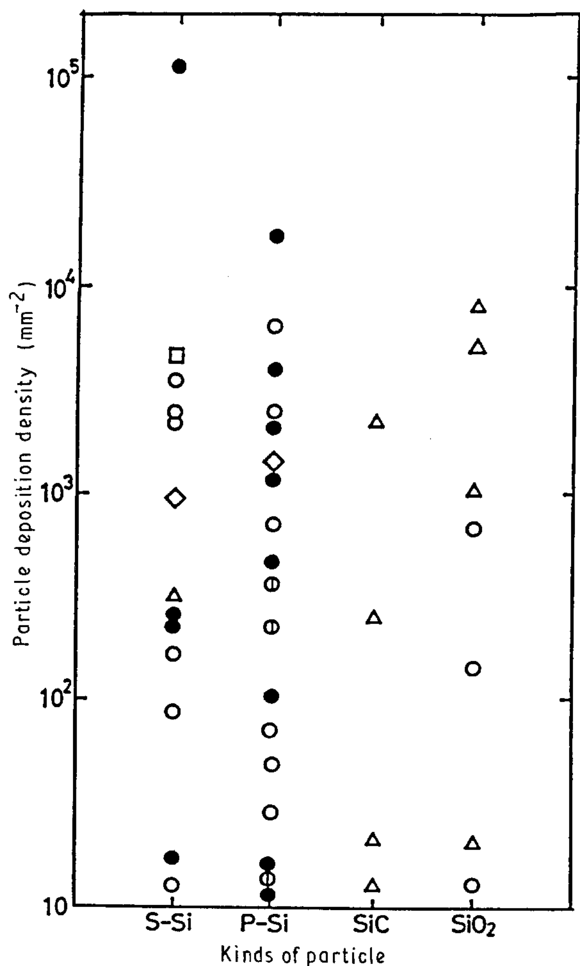


Figure 6 Particle deposition density obtained on the particle surface. Particle size: (○ ⦶ ●) 2000–4000 μm, (□) 500–1000 μm, (△) 250–500 μm, (◇) 149–250 μm. Reaction time: (○ □ △ ◇) 1 h, (⦶) 2 h, (●) 5 h.

in Fig. 6. The deposition particle density was almost independent of the particle size, the reaction time and the kind of particle. Careful observation of the surface of the particle substrate showed that the particle surface for the high deposition density was relatively lusterless; on the other hand, the particle surface for the low deposition density was quite glossy. It is considered that the particle deposition density is strongly dependent on the surface physical characteristics of particle substrates.

3.2. Deposition on the pretreated particles

S-Si particles of 250–500 μm were fluidized for 5 h at a gas velocity of 60 cm s^{-1}. The deposition experiments were performed on the pretreated particles with a

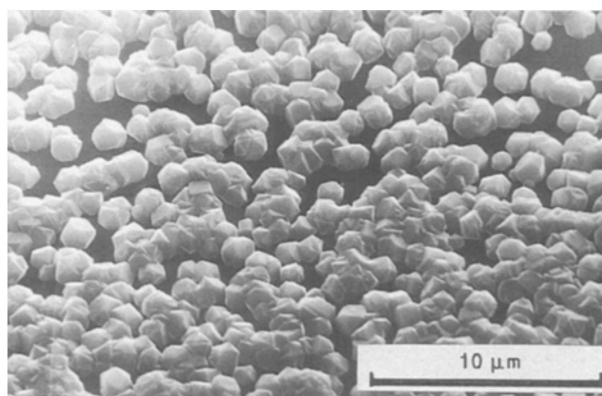
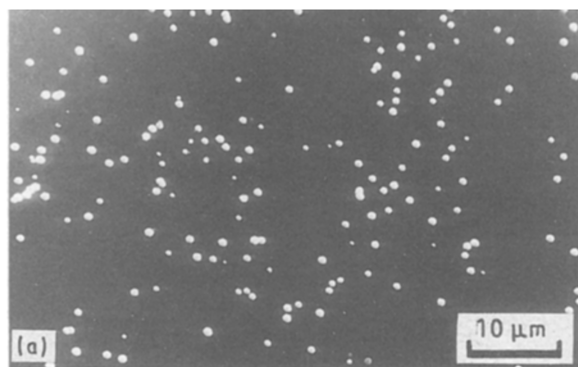
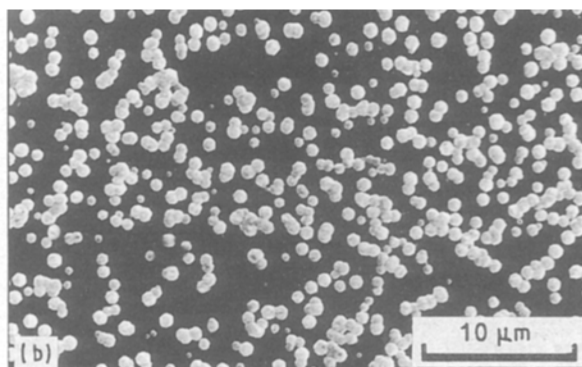
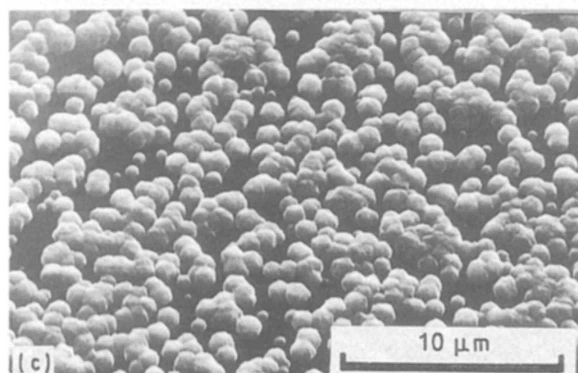


Figure 7 SEM image of diamond particles deposited on the pretreated S–Si particle. Pretreatment time 5 h, reaction time 1 h, reaction pressure 30 torr, input power 200 W, particle substrate size 250–500 μm.







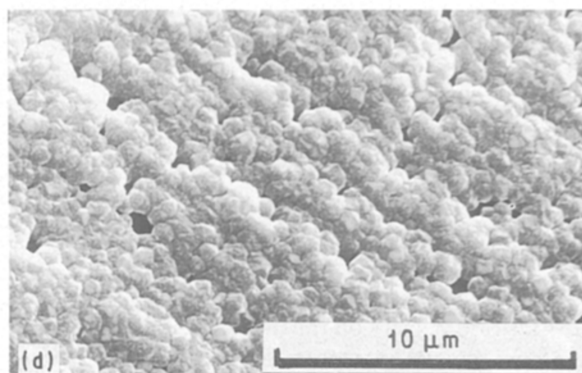


Figure 8 SEM images of deposits on S–Si particles pretreated in a fluidized bed. Pretreatment time: (a) 15 min, (b) 1 h, (c) 5 h, (d) 10 h. Particle substrate size 250–500 μm, reaction time 1 h, reaction pressure 30 torr, input power 200 W.

deposition time of 1 h. A scanning electron micrograph of deposits is shown in Fig. 7. The particle deposition density was enormously increased by the fluidized bed pretreatment and fine particles were uniformly deposited all over the surface of the particles. In a previous study [8], we investigated the effect of the collision of particles with the silicon wafer surface on the nucleation of diamond and found that in the case of the collision of SiC particles with the silicon wafer, to induce nucleation of diamond it was necessary for the particles to collide with the silicon wafer surface with a kinetic energy of over 10^{-9} Nm. It would appear that particles collide with each other with an appropriate kinetic energy in the fluidized bed. Such a collision in the fluidized bed leads to an increase in the active site density for diamond crystallization.

The particle deposition density on the pretreated particle was dependent on the pretreatment time. The results obtained are shown in Fig. 8. The particle deposition density for the sample pretreated for 10 h was high enough to cover the particle surface and it was thus not possible to determine the particle deposition density. Therefore, the reaction time was shortened to 0.5 h for the samples pretreated for over 10 h. The particle deposition densities obtained are shown in Fig. 9. The deposition density increased with increasing pretreatment time and reached about $10^7\,mm^{-2}$ at 15 h. We have already found that the particle deposition density on silicon wafer pretreated by the collision of SiC particles was predominantly dependent on the number and strength of the collisions [8]. It is thought that the increase in the deposition density with pretreatment time is due to the increase in the number of the collisions.

P-Si, quartz and SiC particles were pretreated in the fluidized bed for 1 h at the fluidizing gas velocity of $60\,cm\,s^{-1}$. The deposition was carried out on pretreated particles for 1 h. Fig. 10 show scanning

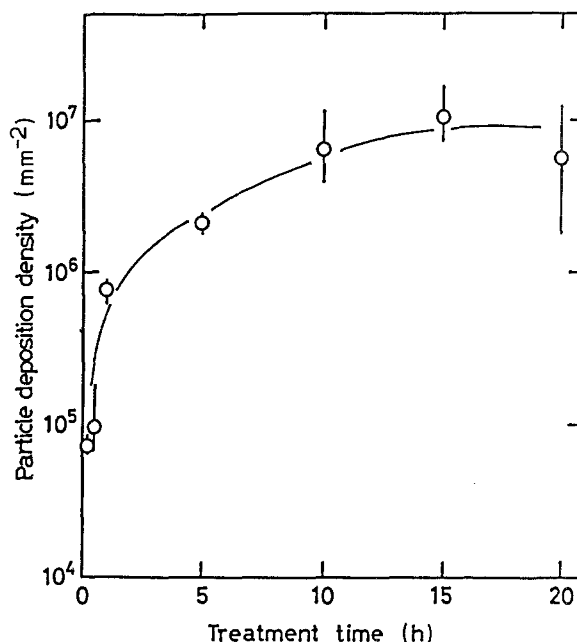


Figure 9 Effect of pretreatment time on particle deposition density. Particle substrate S–Si; particle substrate size 250–500 μm; reaction pressure 30 torr; input power 200 W; fluidizing gas velocity, $u_g = 60\,cm\,s^{-1}$.

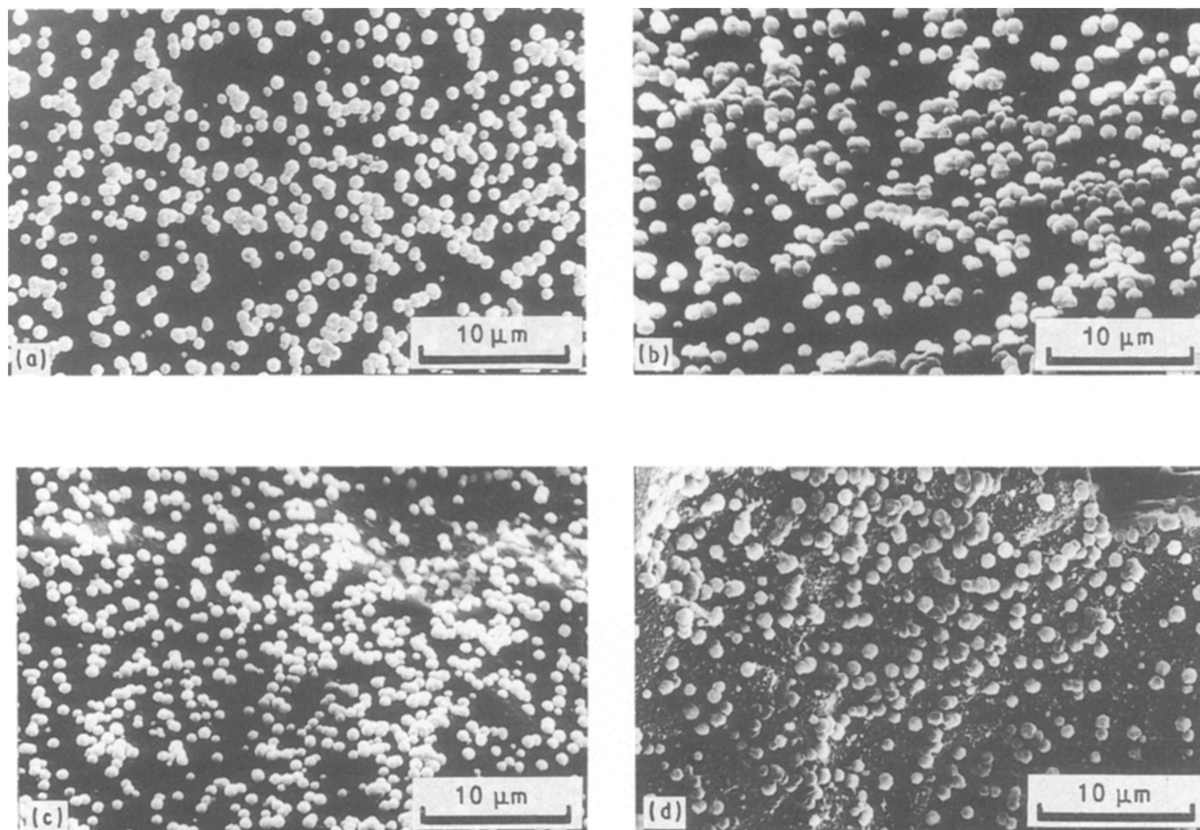


Figure 10 SEM images of diamond particles deposited on pretreated particles. Particle substrate: (a) S–Si, (b) P-Si, (c) SiC, (d) SiO_2. Pretreatment time 1 h, reaction time 1 h, reaction pressure 30 torr, input power 200 W, particle substrate size 250–500 μm.

electron micrographs of deposits on the pretreated particles. A high deposition density of about 10^6 mm^{-2} was observed for all kinds of particle examined. The deposition density, morphology and diameter of fine diamond particles synthesized on P-Si, SiO_2 and SiC particles were similar to those observed on S-Si particles. It was found that the fluidized bed pretreatment of particles was very effective in creating nucleation sites on the particle surface for all the kinds of particle examined.

4. Conclusions

The chemical vapour deposition of diamond on particle substrates was carried out using four kinds of non-diamond particles (single- and, poly-crystal silicon, quartz and SiC particles).

The following conclusions were drawn.

1. Fine diamond particles are deposited on non-diamond particle surfaces.

2. The particle deposition density on the untreated particle substrates was strongly dependent on the physical characteristics of the particle surface; its value ranged from 10–10^5 mm^{-2} for each particle substrate.

3. The pretreatment of the particle surface in the fluidized bed was quite effective for the nucleation of diamond. A deposition density of about 10^7 mm^{-2} was obtained on single-crystal silicon particles treated for 15 h.

References

1. J. C. ANGUS, H. A. WILL and W. S. STANKO, *J. Appl. Phys.* **39** (1968) 2915.
2. B. V. SPITSYN, L. L. BOUILOV and B. V. DERJAGUIN, *J. Cryst. Growth* **52** (1981) 219.
3. S. MATSUMOTO, Y. SATO, M. TSUTSUMI and N. SETAKA, *J. Mater. Sci.* **17** (1982) 3106.
4. M. KAMO, Y. SATO, S. MATSUMOTO and N. SETAKA, *J. Cryst. Growth* **62** (1983) 642.
5. Y. SAITO, H. SATO, H. TANAKA and H. MIYADERA, *J. Mater. Sci.* **24** (1989) 293.
6. Y. MITSUDA, Y. KOJIMA, T. YOSHIDA and K. AKASHI, *ibid.* **22** (1987) 1557.
7. S. YUGO and T. KIMURA, in "Abstracts of First International Conference on The New Diamond Science and Technology", Japan New Diamond Forum, Keidanren Kaikan, Tokyo, October 1988, p. 130.
8. T. TAKARADA, F. EBIHARA, H. MATSUSHIMA and K. KATO, *Kagaku Kogaku Ronbunshu* **17** (1991) 796.
9. T. TAKARADA, H. TAKEZAWA, K. TAMURA and K. KATO *ibid.* **18** (1992) 122.
10. S. P. CHAUHAN, J. C. ANGUS and N. C. GARDNER, *J. Appl. Phys.* **47** (1976) 4746.
11. M. KAMO, Y. SATO and N. SETAKA, *J. Chem. Soc. Jpn* (1984) 1642.

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