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Enhancement of Diamond Nucleation Density by Pretreatment in Hexane Medium

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A pretreatment of the substrate is needed to synthesize continuous diamond film on silicon or metal. The pretreatment is generally carried out by diamond powder dispersed in acetone or alcohol under ultrasonic irradiation. In this paper we used hexane as the dispersion media, and synthesized the diamond on silicon by conventional MPCVD. The grain size of the continuous film whose substrate was treated in hexane under ultrasonic irradiation was successfully reduced to < 100nm. The corresponding nucleation density was enhanced to > 10^{10}/ cm^2. The product was beautifully colored by the interference of light in the visible range. When the substrate was treated in ethanol , the density was $10^8/cm^2$. These diamond films were observed by field emission scanning electron microscopy (FE-SEM).

1. INTRODUCTION

The density of diamond nuclei is decided in the initial nucleatioon stage. Substrates must be treated by hard abrasives, such as diamond powders prior to the diamond deposition to form a continuous film. The grain size of a continuous polycrystalline film formed this way is in the range of a few to a few tens of micrometers. In other words, the nucleation density is less than $10^8/cm^2$. It is hard to make a continuous film smoother than the grain size, so the application of this polycrystalline film to optical devices is rather limited since it is not transparent to visible light. The synthesis of a nanostructured polycrystalline diamond with a grain of less than 100nm, ie. a nucleation density of > $10^{10}/cm^2$, has been investigated. If films with this nucleation density can be achieved, optical and mechanical properties of synthetic diamond would be improved, and the application would be much enhanced.

Takarada *et al.*[1,2] reported that the nucleation density was much enhanced when the substrate was treated with diamond powder falling down to it. Erz *et al.*[3] used different diamond powder with grain size in the range 0.01-3 μm to enhance nucleation. Nucleation density up to 3×10^{10} $/cm^2$ were achieved by polishing the substrate with 10 nm diamond powder.

In this paper we succeeded in enhancement of diamond nucleation density to > $10^{10}/cm^2$ with simply changing from an ethanol medium to hexane under the same ultrasonic irradiation.

Table 1
Experimental Conditions

Material	CH4 / H2 0.5%
Total Flow Rate	100.5 ccm
Total Pressure	40 Torr
Microwave Power	400 W

2. EXPERIMENTAL

A mirror-polished (100) silicon wafer was cut to 10 mm x 10 mm, and pretreated with 8-16 μm diamond powder under ultrasonic irradiation after Yugo *et al.* [4] One gram of diamond powder was dispersed in 30 cc of ethanol or hexane, which was contained in a 50 cc bottle with a screw cap. The silicon wafer was placed in a bottle containing this mixture, and irradiated by ultrasound for 30 min. The treated substrate was repeatedly washed in the same liquid under ultrasonic irradiation. Finally, the substrate was dried in atmosphere for a few minutes, and placed in MPCVD reactor. The details of the reactor system are shown in the previous paper[5]. The synthesis condition is summarized in Table 1. The deposited product was characterized by Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi S-900).

3. RESULTS AND DISCUSSION

A significant difference was observed when the substrate was pretreated for longer than 30 min in our ultrasonic system. FE-SEM pictures of the deposited product after 30min pretreatment are shown in Fig.1. The deposition time was 60 min. On the substrate treated in the ethanol medium, a continuous film was not formed. The longer deposition lead to a continuous film with a grain size of ~1 μm. The corresponding grain density was $\sim 10^8$ /cm^2, which was within the values reported so far [6]. In contrast, a continuous film with a grain size of ca.100 nm was synthesized on the substrate treated in the hexane medium after 60 min deposition. In this stage the grain density is kept at $\sim 10^{10}$ /cm^2. The FE-SEM view was shown in Fig. 2. Because of the interference of light in the visible range, it was beautifully colored in blue. The color changed depending on the deposition period, suggesting the homogeneity of the product thickness on the substrate. Takarada et al. [1,2] and Erz et al. [3] succeeded in the enhancement of diamond nucleation density with respectively diamond powder falling down on the substrate and using 10 nm diamond powder to polish it. Simply changing the dispersion medium from ethanol to hexane a similar enhancement effect was attained, and a very flat thin film was synthesized.

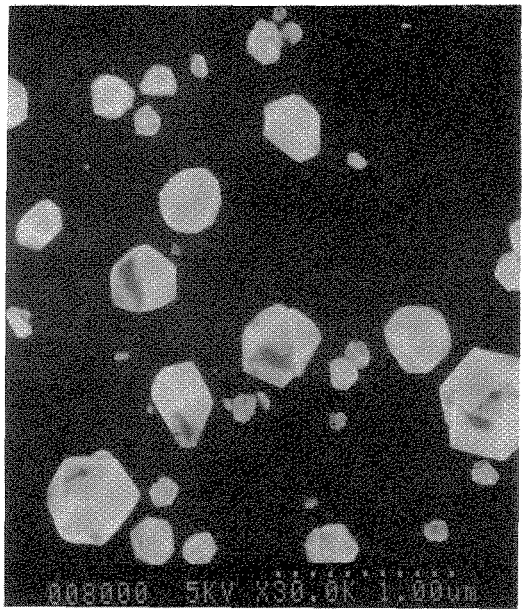

Fig. 1 FE-SEM photograph of diamond synthesized on substrate treated in ethanol medium.

Fig. 2 FE-SEM photograph of diamond synthesized on substrate treated in hexane medium.

4. CONCLUSIONS

The nucleation density is much enhanced to > $10^{10}/cm^2$ via controlled surface pretreatment in hexane medium. The grain size of the continuous film was successfully reduced to < 100nm. The product was beautifully colored by the interference of light in the visible range. When the substrate was treated in ethanol , the density was $10^8/cm^2$.

REFERENCES

1. T. Takarada, T. Takeawa, K. Tamura, N. Nakagawa, and K. Kato, Kagaku Kogaku Ronbunshu, 18 (1992) 122.
2. T. Takarada, K. Tamura, H. Takezawa, N. Nakagawa, and K. Kato, J. Mater. Sci. 28 (1993) 1545.
3. R. Erz, W. Dotter, K. Jung and H. Ehrhardt, Diamond and Related Materials, 2 (1993) 449.
4. S. Yugo, T.Kimura, H. Kanai, and Y. Adachi, Mater. Res. Soc. Symp. Proc. 97 (1987) 327.
5. T. Okubo, S. Ikari, K. Kusakabe, and S. Morooka, J. mater. Sci. Lett. 11 (1992) 460.
6. K. Kobashi, K. Nishimura, Y. Kawate, and T. Horiuchi, Phys. Rev. B38 (1988) 4067.