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Diamond growth on $CoSi_2$/Si by bias-enhanced microwave plasma chemical vapor deposition method

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Abstract

Diamond was grown on polycrystalline $CoSi_2$/Si substrates by bias-enhanced microwave plasma chemical vapor deposition. Both of the positive and negative biasing effects were investigated by microstructural characterization. It has been found that nucleation density can reach $\sim 10^9$ cm^{-2} with positive biasing, much higher than with negative biasing. Cross-sectional transmission electron microscopy shows that diamond deposited by positive biasing grows on a relatively smooth $CoSi_2$ surface, while the etching effect of ion bombardment during negative biasing results in a rough $CoSi_2$ surface. The diamond morphology obtained with negative bias has a flat surface with a strong (1 0 0) texture. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Plasma-assisted CVD; Electron microscopy; Diamond; Nucleation

1. Introduction

Diamond has many excellent physical and mechanical properties such as extreme hardness, high thermal conductivity, wide bandgap and optical transparency. For the realization of electronic diamond devices, it is important to synthesize the heteroepitaxial diamond films. It has been known that diamond can be grown by microwave plasma chemical vapor deposition (MPCVD) and the nucleation density of diamond could be increased by bias-enhanced nucleation (BEN) method [1–5]. The BEN method can lead to the formation of a heteroepitaxial film for which a high density of nucleation of diamond on substrate is often a necessity.

Diamond growth on Si has been reported. It is usually found that a β-SiC interlayer is formed before the diamond growth [5]. In the case of cemented carbides, such as WC–Co, the dissolution of carbon into the substrate induces graphitization of the deposit [6]. Si is a strong carbide former, while Co is hardly able to form a carbide with C in chemical vapor deposition (CVD). It will be of interest to know the role of Co and Si effects on nucleation. In the present study, diamond films were synthesized on $CoSi_2$ substrate by MPCVD with BEN method in a mixed gas of CH_4 and H_2. $CoSi_2$ is a stable phase of silicide in Co–Si binary system, and is an important material in microelectronic devices. Since lattice mismatch of $CoSi_2$ with Si is 1.2%, it is possible to obtain a highly oriented or epitaxial film of $CoSi_2$ on Si. From the structural point of view, diamond growth on $CoSi_2$ could have a similar behavior to that on Si. Previous work by Arnault et al. [7] shows that diamond deposited on $CoSi_2$ by hot-filament CVD is preceded by the formation of a SiC layer. Gu et al. [8] have recently reported that high-quality textured diamond films can be grown on $CoSi_2$ with BEN pretreatment. Here, we demonstrate that the positive biasing effect on diamond deposition is different from the negative one through microstructural characterization.

2. Experimental

A $CoSi_2$ layer formed on Si (1 0 0) wafer was used as the substrate. $CoSi_2$ layers of 100 nm thickness were formed by electron beam evaporation of Co on Si, followed by rapid thermal annealing (RTA) at 800°C for 1000 s. A tube MPCVD reactor was used to deposit diamond. Before inserting into the MPCVD reactor, the substrates were cleaned by acetone, followed by removal of oxides by HF. Mixture of CH_4 and H_2 was used as the gas source and d.c. power supply was used to create the bias. The substrates were put onto a Mo holder. A tungsten needle of diameter 0.5 mm or a 3 mm diameter Mo disk was used as the electrode. The corresponding applied bias voltage on the substrate was in the range −150 to +300 V. After biasing, all the samples received the same growth conditions for 4 h. The experimental condition for deposition is listed in Table 1. Microstructural

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Table 1
Experimental parameters

	Power (W)	Pressure (Torr)	Concentration (%), CH_4 in H_2	Bias voltage (V)	Time (min)
H_2 plasma etching	500	20	0	0	20
Carburization	500	20	2	0	60
BEN	500	20	2	−150 to +300	10–15
Growth	500	20	1	0	240

characterization was performed by X-ray diffractometry (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Cross-sectional TEM specimens were prepared by gluing the diamond face with a glass slide, followed by mechanical grinding and ion milling.

3. Results and discussion

XRD patterns reveal that the Co films were reacted with Si into $CoSi_2$ films after RTA. Though the $CoSi_2$ films are polycrystalline, they have (1 0 0) strong preferred orientations on Si (1 0 0) substrates.

3.1. Negative biasing

SEM image in Fig. 1a shows the distribution of diamond particles on $CoSi_2$/Si (0 0 1) substrate with biasing at −150 V. Smooth (1 0 0) facets are clearly seen on each particle in Fig. 1b, indicating that diamond is highly oriented in (1 0 0) texture. In some cases, secondary diamond nuclei on the facets were also observed. Interestingly, deposition did not result in a continuous film. The density of diamond particles is estimated to be larger than $1 \times 10^6\,cm^{-2}$. This is an order of magnitude lower than that in diamond deposition on Si using the same experimental condition.

SEM observation reveals that $CoSi_2$ surfaces on Si uncovered by diamond were very rough, implying that $CoSi_2$ might be modified by biasing. Cross-sectional TEM examination on the specimen after diamond deposition shows that $CoSi_2$ has been etched into a cone shape as shown in Fig. 2.

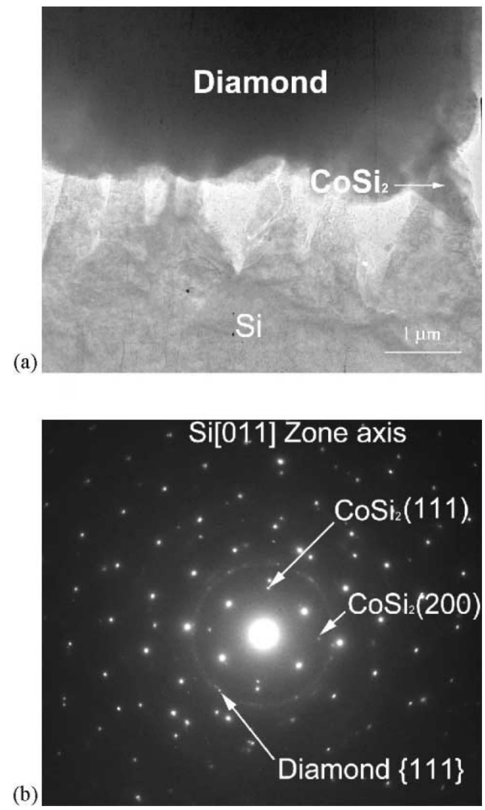

Fig. 2. (a) Cross-sectional TEM micrograph showing diamond deposited on $CoSi_2$ with −150 V bias voltage and (b) the corresponding selected area electron diffraction pattern showing diamond {1 1 1} ring.

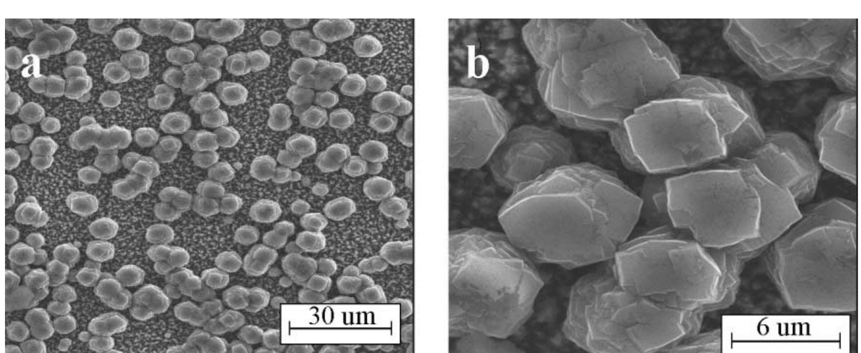

Fig. 1. SEM images showing (1 0 0) textured diamond films grown on $CoSi_2$/Si (1 0 0). Magnification: (a) ×1000; (b) ×5000.

The etching effect is mainly caused by ion bombardment during biasing. The diamond particles are seen on top of the $CoSi_2$ cones. The diamond {1 1 1} ring in selected area diffraction pattern of Fig. 2b demonstrates that diamond sitting on those cones in Fig. 2a image is of polycrystalline nature. No interfacial SiC layer can be observed between diamond and $CoSi_2$, implying that diamond may directly nucleate on $CoSi_2$. Also, it is noted that the Si substrate has been etched. Hence, the strong etching effect of ions results in a small volume of $CoSi_2$ left on top of the cones.

3.2. Positive biasing

XRD pattern in Fig. 3 obtained from a sample pretreated with bias voltage of +300 V, shows a strong (1 1 1) diamond peak, indicating diamond is in (1 1 1) preferred orientation. SEM micrograph in Fig. 4 shows that a continuous film of diamond has been formed. The surface of the diamond film is not smooth with grain morphology of (1 1 1) facets. The grain size is rather small compared with those deposited with negative biasing. The nucleation density of diamond is estimated in the order of $10^9\,cm^{-2}$. The enhanced nucleation density of diamond on Si with positive biasing has also been observed consistent with previous reports [9]. TEM micrograph with the corresponding electron diffraction pattern in Fig. 5 shows that diamond was grown on $CoSi_2$. The interface between diamond and $CoSi_2$ is relatively smooth, implying that the $CoSi_2$ surface has not suffered the etching effect during biasing. Also, no apparent interlayer between diamond and substrate can be seen. With positive biasing, most of the charged particles bombarding the substrate are electrons, which may have a negligible effect on the surface. However, electrons of the sufficiently high energy obtained by the applied bias voltage might result in an increase in the amount of carbon-containing radicals near the surface to enhance diamond nucleation.

The higher density of diamond deposited with positive biasing than negative one can be attributed to the smoothness of substrate surface. In negative biasing, the surface is very rough, approximately with one cone per micrometer. Since the cones are likely the nucleation sites for diamond, the number of cones available will limit diamond nucleation. In contrast, $CoSi_2$ surface remains to be smooth during positive biasing, which allows diamond nucleate

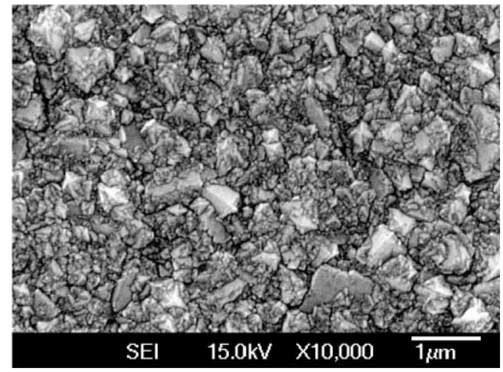

Fig. 4. SEM micrograph showing the morphology of diamond film deposited with positive biasing at +300 V on $CoSi_2$/Si (1 0 0) substrate.

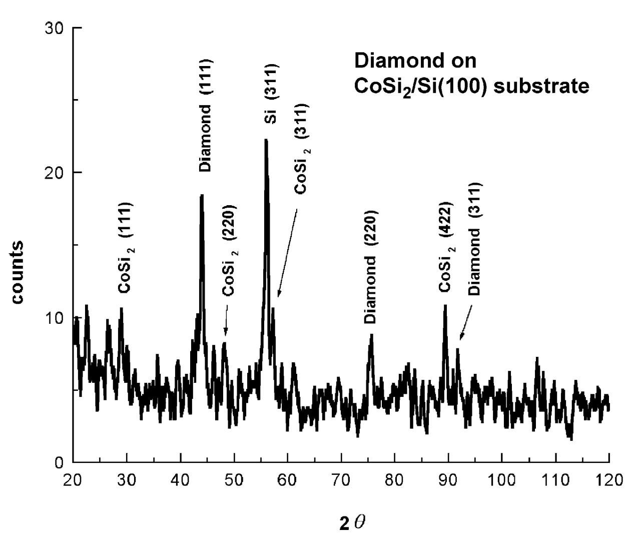

Fig. 3. XRD pattern showing (1 1 1) texture of diamond film deposited with positive biasing at +300 V on $CoSi_2$/Si (1 0 0) substrate.

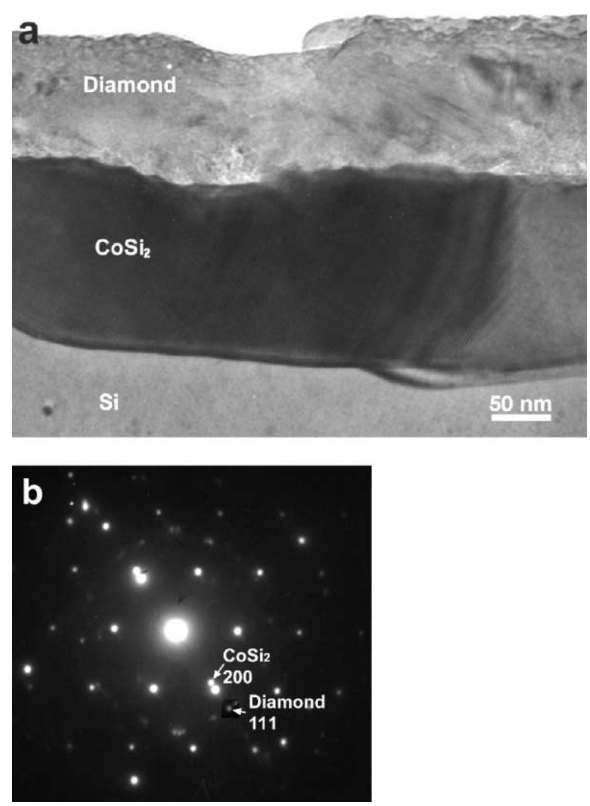

Fig. 5. (a) Cross-sectional TEM micrograph showing diamond deposited with positive biasing at +300 V on $CoSi_2$/Si (1 0 0) substrate and (b) the corresponding selected area electron diffraction pattern showing diamond (1 1 1) ring.

without the site limitation. Similar behavior on Si has also been observed.

4. Conclusions

Diamond deposition on $CoSi_2$/Si substrates with pretreatment by biasing in positive and negative voltages has been investigated. Both of the positive and negative biasing enhance the nucleation density of diamond. However, negative biasing results in a rough surface of the substrate due to etching of ion bombardment. In contrast, positive biasing gives a relative smooth surface of substrate on which diamond can be grown. As a result of surface smoothness, the nucleation density of diamond obtained with positive biasing can reach $10^9\,cm^{-2}$, about two orders of magnitude higher than that obtained with negative biasing. The diamond morphology in the negative-biased film has a flat surface with a strong (1 0 0) orientation, while that in the positive one is relatively rough with (1 1 1) facets.

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