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Diamond deposition on Au/amorphous Si thin films

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Abstract

Au/amorphous $Si/SiO_2/Si$ structure was used as substrate for diamond deposition by microwave plasma CVD. The Au–Si phase diagram shows a eutectic point at 363 °C. At deposition temperatures of 700–800 °C, the Au and amorphous Si films were alloyed as liquid during deposition, which resulted in formation of an array of single crystalline Si whiskers. Microstructural characterization shows that the Si whiskers have a diameter in the range of 50 nm–5 μm with facet on the top surface. The Si whiskers are shown to be oriented along ⟨311⟩ directions. Diamond particles deposited are found *only* on top of the Si whiskers. The diamond particles can be either of polycrystalline or single crystalline characteristics.

Keywords: Diamond crystal; Chemical vapor deposition; Morphology

1. Introduction

Low temperature and low pressure chemical vapor deposition (CVD) of diamond has been intensively studied for the last two decades. Most of the studies have attempted to synthesize diamond in form of particles and thin films on various solid substrates. Roy et al. have reported that diamond can be precipitated from carbon-rich metallic liquids in a microwave plasma below 1 atm [1]. Fan and Hou have demonstrated that diamond can be grown on liquid substrates using CVD [2]. Here, we report a novel method for diamond formation with an array of self-formed Si whiskers using a thin film of Au/amorphous Si bilayer as the substrate, which can react into a liquid alloy at the deposition temperature in CVD environment. According to Au–Si binary phase diagram, there is a eutectic point at 363 °C, and both Au and Si have negligible solid solubility within each other [3]. The results show that diamond *only* forms on top of Si whiskers. In contrast, Givargizov et al. recently demonstrated that sharp Si whisker arrays were formed using patterning technique by microelectronic processing followed by vapor–liquid–soild (VLS) method, upon which diamond deposition was carried out [4–6]. They found that diamond particles formed on the tip and shank of Si whiskers. Such a structure may be utilized for field emission devices and micro-electromechanical systems.

2. Experimental

Deposition of diamond was carried out in a tubular microwave plasma CVD reactor. The substrates were prepared as follows. A 200-nm thick SiO_2 were grown on Si(001) wafer, followed by deposition of an amorphous Si (a-Si) film in 65 nm thickness. Both SiO_2 and a-Si were formed by using plasma-enhanced CVD. Then, an Au film of 130 nm was deposited on a-Si by electron-beam evaporation method. The thickness ratio of the a-Si and Au films corresponding to 5.6 wt.% Si composition would allow them to alloy into a liquid solution above 700 °C according to the Au–Si phase diagram in Fig. 1 [3].

Before diamond deposition, hydrogen plasma was applied onto the substrate to heat Au and a-Si into liquid solution. After hydrogen plasma heating for 10 min, CH_4 gas in 0.33–10% concentration was flowed into the reactor for diamond deposition for a period from 15 min to 4 h. In some cases, a positive bias pretreatment on the substrate before diamond growth was carried out with 4% CH_4. In the bias condition, a positive bias voltage in the range of 100–300 V was applied for 15 min to a counter electrode of Mo, which were a few millimeters above the substrate. The typical

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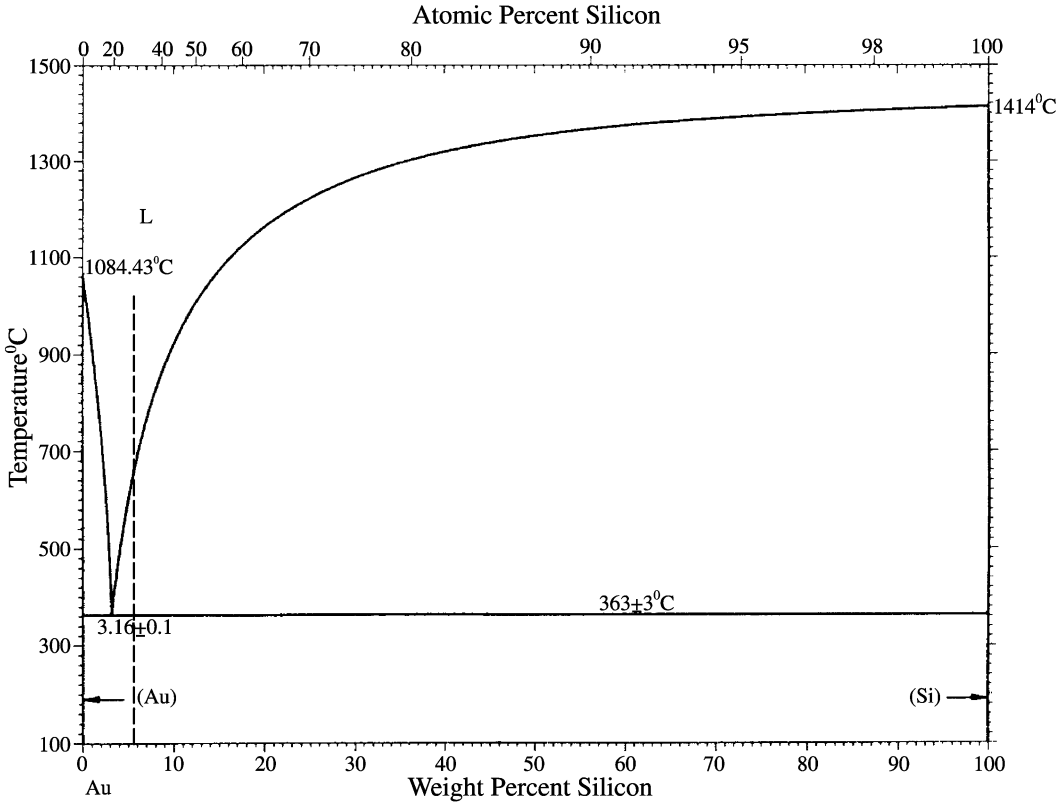

Fig. 1. Au–Si phase diagram [3].

deposition parameters for diamond growth were pressure of 20–30 Torr, substrate temperature at 800–900 °C as measured by an optical pyrometer, total flow rate of 300 sccm, and power in 500 W. The detailed experimental conditions are listed in Table 1. The specimens were then characterized by Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The 532 nm line of an Argon ion gas laser with 20 mW power was employed for acquisition of Raman spectra.

3. Results and discussion

Fig. 2 shows a typical SEM micrograph from the peripheral region of a sample which was around the edge of plasma ball where the temperature was relatively low in comparison with the central region of the sample covered by the plasma. X-Ray energy dispersive spectroscopy shows that the area consists of Au and Si. The lamella microstructure of colonies in dark and bright contrast shows the typical characteristics of eutectic solidification, indicating that the Au and a-Si films had been mixed into a liquid alloy during deposition. The typical Raman spectrum shown in Fig. 3a from the deposited samples reveals the characteristic diamond peak at 1332 cm^{-1}, demonstrating that diamond indeed

Table 1
Experimental conditions for diamond deposition

Stage	Heating	Bias	Growth
Power, W	500	500	500
Pressure, Torr	20	20	20
CH_4 in H_2, %	0	4	0.33–10
Flow rate, sccm	300	300	300
Bias voltage, V	0	+100–+300	0
Time, min	10	0, 15	0–240

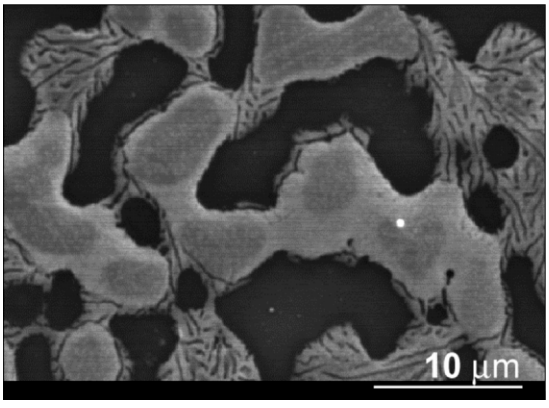

Fig. 2. SEM micrograph from area close to the edge of plasma ball, showing the eutectic lamella microstructure in colonies. Deposition conditions: bias 200 V/4% CH_4 and growth 0.66% CH_4/15 min.

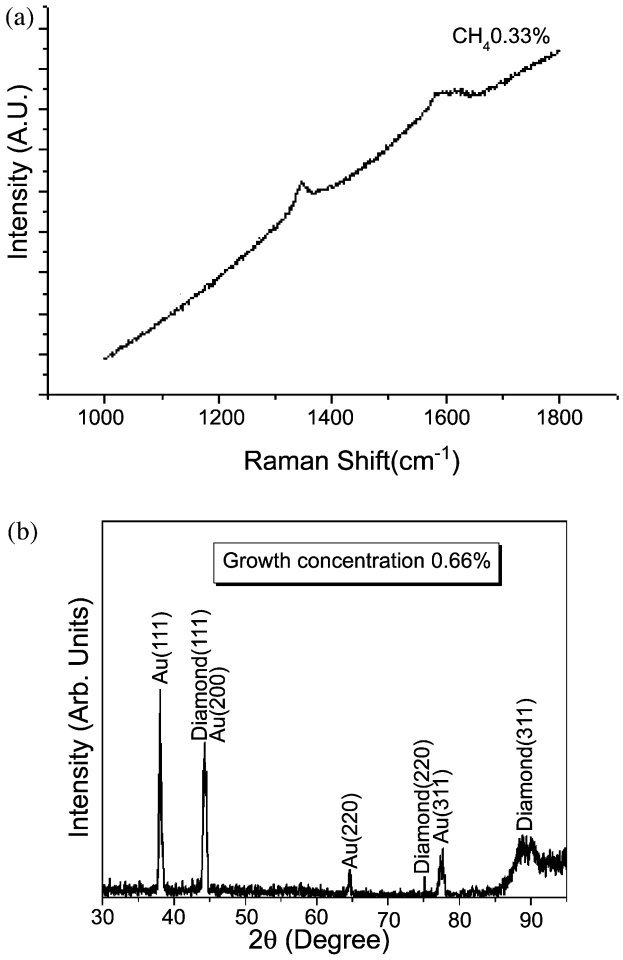

Fig. 3. (a) Raman spectrum showing diamond peak at 1332 cm^{-1}. Deposition conditions: bias 200 V/4% CH_4 and growth 0.33% CH_4/4 h. (b) XRD pattern showing diamond peaks. (Note that the actual diamond 111 peak (43.93°) is very close Au 200 (44.39°). However, the intensity ratio among different Au peaks suggests the actual Au 200 peak height should be lower than the overlapped one.) Deposition conditions: bias 200 V/4% CH_4 and growth 0.66% CH_4/4 h.

has been deposited. Further evidence of diamond formation comes from the result of XRD as shown in Fig. 3b. The surface morphology after deposition for 15 min bias treatment using 4% CH_4 followed by further growth for 15 min with 0.33% CH_4 is shown in Fig. 4a. It is observed that faceted diamond particles in bright contrast were grown only on top of cone-like Si whiskers, which exhibit as an array. The Si whiskers have a height of approximately 200 nm and a diameter in the range of 100–500 nm at the bottom. The diamond size is somewhat larger in the range of 200–800 nm. Most of Si whiskers are capped with one single diamond particle, while a few of them have multiple diamond particles. A number of Si islands in a size of a few micrometers are also seen in dark contrast. Similar morphology is also observed from samples deposited by different bias conditions. A particular case deposited without bias is shown in Fig. 4b, which shows a diamond particle of ~400 nm size with the shape of faceted polyhedron on a Si whisker. On the substrate surface, no diamond was found, even if the surface with bias treatment (Fig. 4a) is seen to be rough probably due to the etching effect. The density of Si whisker and diamond is found to increase with bias voltage. With bias voltage increasing from 0 to 300 V, the density is increased from 10^5 cm^{-2} (without bias) to 10^8 cm^{-2}. The size of diamond and Si whisker can be varied from 50 nm to 5 μm depending on the deposition conditions. In general, the size decreases with the nucleation density as the bias increases from 100 to 300 V. TEM observation in cross-section reveals that these Si whiskers are all oriented along ⟨311⟩ direction. In Fig. 5, the bright-field TEM micrograph obtained from a biased specimen shows a Si whisker covered with a diamond particle. The corresponding selected-area diffraction pattern in Si ⟨112⟩

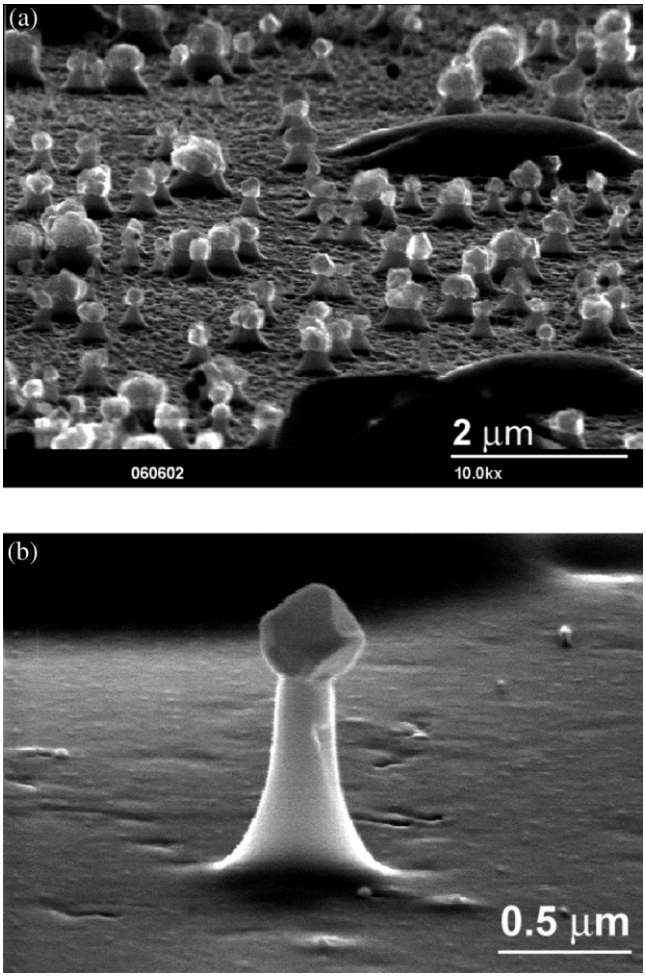

Fig. 4. SEM micrographs showing (a) diamond particles (bright contrast) on top of Si cones (Deposition conditions: bias 200 V/4% CH_4 and growth 0.33% CH_4/15 min); and (b) a single crystalline diamond on Si (Deposition conditions: no bias treatment, 4% CH_4/30 min and 0.33% CH_4/30 min).

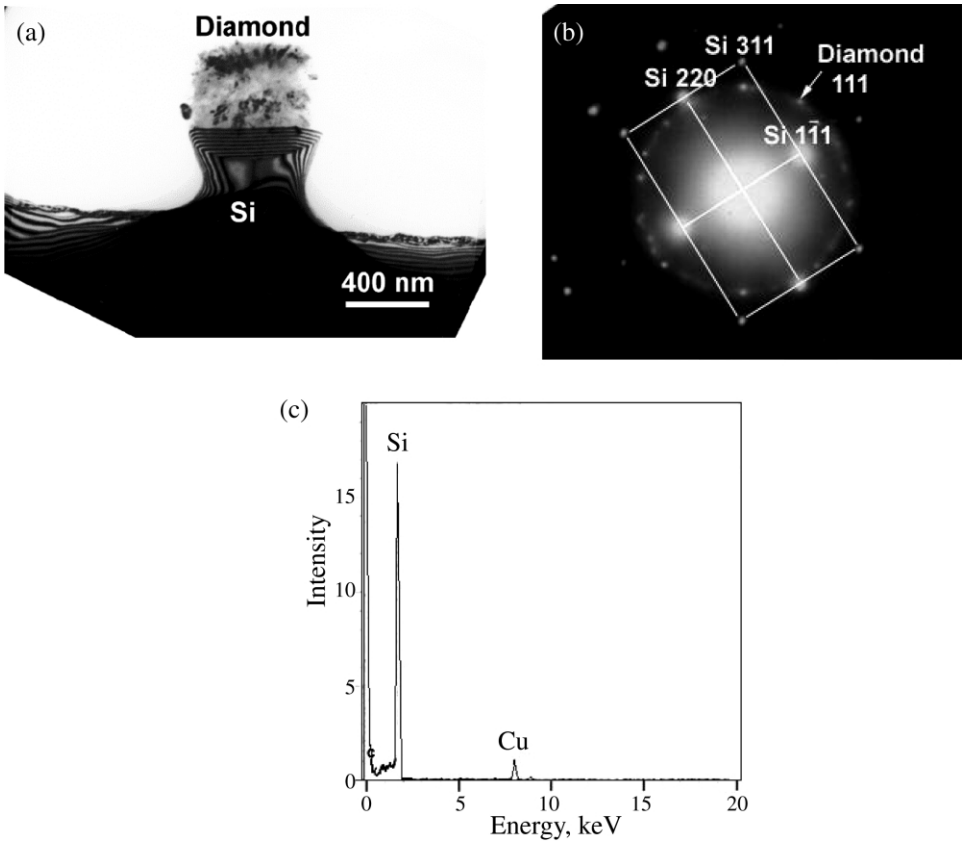

Fig. 5. (a) TEM micrograph showing polycrystalline diamond on a Si whisker; and (b) the corresponding diffraction pattern showing Si reflections in ⟨112⟩ zone with diamond 111 ring. (c) EDX spectrum obtained from the Si whisker showing no Au signal detected. Deposition conditions: bias 200 V/4% CH_4 and growth 0.66% CH_4/15 min.

orientation and the image contrast of thickness fringes from the Si whisker exhibit single-crystalline characteristics, demonstrating that the Si whisker is actually a single crystal. The ring in the diffraction pattern is diamond 111 reflections as a result of polycrystalline diamond. Also, the whisker is found to be flat on the top when the interface between diamond and Si was tilted in the edge-on orientation, which is coincident with Si ⟨112⟩ zone axis. Therefore, the whisker is grown along ⟨311⟩, and the facet is likely parallel to {311}. No dislocations are seen in the Si whisker. TEM examination of a few of deposited specimens with different processing parameters shows that all Si whiskers observed have the same characteristics as described above. TEM also shows that the diamonds are only deposited on top of those Si whiskers rather than on the elsewhere in consistence with SEM observations. The deposited diamond can be polycrystalline or nearly single crystalline as evidenced by selected area electron diffraction (SAED). The diamond in Fig. 5 is polycrystalline deposited in growth stage with 0.66% CH_4, while in Fig. 6 from another TEM specimen deposited with 0.33% CH_4 it is single crystal as can be seen the corresponding diffraction pattern which consists of a diamond pattern in ⟨111⟩ zone axis with Si ⟨110⟩ pattern. Microanalysis from X-ray energy dispersive spectroscopy shows that no Au is left in Si whiskers and diamonds (Fig. 5c). Some well faceted Au particles in micrometer size are found around on the substrate surface, implying that Au has been evaporated from the surface and re-deposited on it.

To understand why the Si whiskers were formed, a few experiments have been carried out in the same conditions used for diamond deposition except that no CH_4 gas was added. SEM examination shows that no Si whisker formed. This suggests that formation of the Si whiskers is strongly related with carbon radicals in the plasma. The carbon radicals could be adsorbed on the liquid surface, so that the surface energy was changed. It is also likely that carbon could be solved in the liquid of AuSi alloy. As the Au was rejected from the liquid, the melting temperature of the AuSi alloy would be raised, resulting in solidification of Si, which might lead to formation of Si whiskers due to the capillary effect. Alternatively, Si etching by the plasma could increase its vapor concentration, providing the necessary source for formation of Si whisker as shown in growth of whiskers by the vapor–liquid–solid mech-

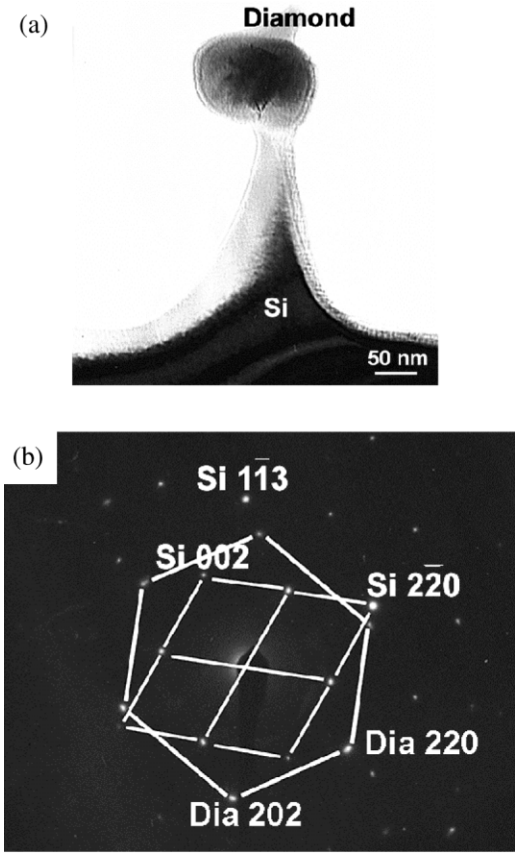

Fig. 6. (a) TEM micrograph showing single-crystalline diamond on Si and (b) the corresponding diffraction pattern showing Si in ⟨110⟩ zone and diamond in ⟨111⟩ zone (Note that the diamond/Si interface is not edge-on). Deposition conditions: bias 200 V/4% CH_4 and growth 0.33% CH_4/15 min.

anism. The behavior in the present study is different from whisker growth by conventional VLS mechanism although Au is used in both cases. In conventional VLS growth of Si whiskers, Si-containing vapor sources are constantly provided and dissolved in the liquid, followed by precipitation at liquid–solid interface [7,8]. In our case, only CH_4 and H_2 gases were flowing into the reactor during deposition. Therefore, the Si resource is limited even if it is from etching effect. Formation of the Si 311 facet has been reported when the Si surface is contaminated with carbon during crystallization of Si [9,10]. Also, 311 facets have been observed in Si epitaxial growth on Si. Thus, formation of 113 facet on the top surface of a Si whisker might be caused by the carbon radicals in the plasma. It is known that carbon solubility in solid state Si is low, but the solubility in liquid Si can be approximately 1.1 wt.% at 1723 K [11]. Also, it is noted that the maximum equilibrium solubility of C in Au in the eutectic liquid is 4.7 at.% [12]. Therefore, it is reasonable to speculate that carbon concentration is relatively high on the top surface of a Si whisker at which the last drop of existed liquid might dissolve a certain amount of carbon species. As a result, diamond could more easily nucleate on top of the Si whiskers, whereas on the substrate surface there is no diamond nucleation. Since no Au is found with Si and diamond, it is likely that Au had already depleted from the whisker before diamond formation. As the substrate surface remains relatively flat when CH_4 is not added, we can conclude that carbon plays an important role in whisker formation and diamond selective nucleation on top of a whisker surface. Further experiments may help to clarify the exact mechanism.

4. Conclusions

Diamond deposition on Au–Si bilayers has been demonstrated through liquid alloying step using microwave plasma-enhanced CVD method. It has been shown that single crystalline Si whisker arrays in cone-like morphology with {311} facet on the top can form with methane. The top surface of each whisker is capped with diamond.

Acknowledgments

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