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Diamond growth on thin Ti wafers via chemical vapor deposition

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Diamond film was synthesized on thin Ti wafers (as thin as 40 μm) via hot filament chemical vapor deposition (HFCVD). The hydrogen embrittlement of the titanium substrate and the formation of a thick TiC interlayer were suppressed. A very low pressure (133 Pa) was employed to achieve high-density rapid nucleation and thus to suppress the formation of TiC. Oxygen was added to source gases to lower the growth temperature and therefore to slow down the hydrogenation of the thin Ti substrate. The role of the very low pressure during nucleation is discussed, providing insight into the nucleation mechanism of diamond on a titanium substrate. The as-grown diamond films were characterized by scanning electron microscopy (SEM), Raman spectroscopy, and x-ray analysis.

Since Spitsyn et al.'s report of synthesis of diamond from the gas phase,[1] many methods have been developed to grow thin diamond films via chemical vapor deposition (CVD)[2-4] in hopes of utilizing the various applications of CVD diamond films owing to the extraordinary properties of diamond.[5] All these methods involve a nucleation stage and a subsequent growth. To get a high density of nuclei, many measures have been taken to enhance nucleation, such as scratching the substrate surface with fine diamond powder before nucleation,[6] predeposition of carbonaceous precursors of non-diamond carbon,[7] etc. As one of the most promising kinds of substrate, silicon has been under the most intensive research. As a matter of fact, great progress has been made in diamond synthesis on silicon. Yugo et al.,[8] Stoner et al.,[9] and Jiang et al.[10,11] acquired high density nucleation on mirror-polished Si by applying a negative bias to the substrate in a microwave plasma CVD (MPCVD) system and, subsequently, they achieved oriented or heteroepitaxial diamond films.[10-12] In spite of all these successes, however, the nucleation mechanism is not very clear as yet, and needs further study.

One of the main substrates in CVD diamond synthesis, titanium has not been given as much consideration as silicon. However, the super-high Young's modulus (1.05×10^{12} N/m^2) and great acoustic velocity (18.5 km/s) of diamond make it alluring to coat thin Ti films with diamond films for the use in speaker's vibrational membranes to achieve high fidelity acoustics.

Unfortunately, diamond growth on Ti substrates, especially thin Ti films, has not been thoroughly investigated.

One great problem is the severe hydrogen embrittlement of the Ti substrate due to the presence of hydrogen at high temperature during diamond deposition. Under high temperature, titanium greatly absorbs hydrogen to form titanium hydride.[13,14] However, this problem is usually overlooked when thick Ti substrates are used (0.5 mm or more). However, for very thin Ti substrates, e.g., 40 μm thick, it becomes apparent. When hydrogenated, the thin Ti wafers become very fragile and are thus of no use for acoustical applications. The difficulty in getting rapid high density nucleation is another serious problem. It results from the formation of thick interfacial TiC layers.[15] It is more obvious than hydrogen embrittlement when thick Ti substrates are used. Park and Lee[15] have reported that nucleation began only after the TiC interlayers grew to be as thick as 50 μm, and that diamond films became continuous only after >240 min deposition at the substrate temperature of 700 °C, which is a temperature high enough to cause serious hydrogenation of the substrates. It can be inferred that the substrates, if thinner than 50 μm, would have mostly changed into TiC. However, the Ti films used in speakers are usually only several tens of microns in thickness (e.g., 40 μm), so it is necessary to minimize the hydrogenation and suppress the formation of TiC.

In this paper, we report a two-step process to grow high quality diamond films on thin Ti films at as low as 550 °C with little hydrogenation and little TiC formation. In the nucleation step (step I), the pressure was as low as 133 Pa. In the growth stage (step II), oxygen was added to the source gases to lower the deposition temperature, and

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also to lessen the deposition time by increasing the growth rate. The thin Ti wafer retained its primitive elasticity.

A long fused silica tube of 500 mm in length and 140 mm in diameter was used as a deposition chamber. Tungsten wire of 0.2 mm diameter wound into coils of 2.5 mm diameter was used as a filament with its temperature measured by an optical pyrometer. The substrates were 10×15 mm^2 thin Ti wafers (40 μm thick) scratched by 0.5 μm diamond powder, chemically cleaned with acetone in an ultrasonic bath for 10 min, and then mounted on a copper substrate holder. The substrate temperature was measured with a thermocouple (Pt–PtRh), carefully arranged in contact with the backside of the substrate. Meanwhile, cooling water was also used in order to adjust the substrate temperature to a desired value. The filament-substrate distance was fixed at 10 mm. After nucleation in step I, the pressure and temperature were adjusted to the predetermined values. Another sample was also used for nucleation using the same parameters as in step I to determine the SEM morphology of the sample immediately after nucleation. The obtained films were analyzed via SEM, Raman spectroscopy, and x-ray diffraction. Other parameters are listed in Table I.

Figure 1 shows the SEM micrograph of the sample after the 5 min nucleation procedure (step I). The nucleation density is measured to be approximately 10^9/cm^2. The nuclei distribution is relatively uniform over all of the sample surface, as shown in Fig. 1. Accordingly, high density nucleation was achieved within as short a time as 5 min.

Figure 2(a) gives the SEM micrograph of the as-grown diamond film after step II. Evidently, the film is of good crystallinity. The crystallites average about 0.5 μm in size. In addition, it is easy to notice their $\langle 001 \rangle$ orientation from their upward pyramidal shape. This indicates a (001) texture, in agreement with the x-ray diffraction results as discussed below. Figure 2(b) shows the cross-sectional SEM image of the diamond/Ti film tilted at 75°. No obvious TiC interlayer can be seen at such a high magnification. The film thickness is approximately 1.3 μm, giving a growth rate of 0.26 μm/h. This rate is quite low compared with the usual growth rate of 1 μm/h for HFCVD. The reason is a combination of low substrate temperature and low filament temperature during growth,
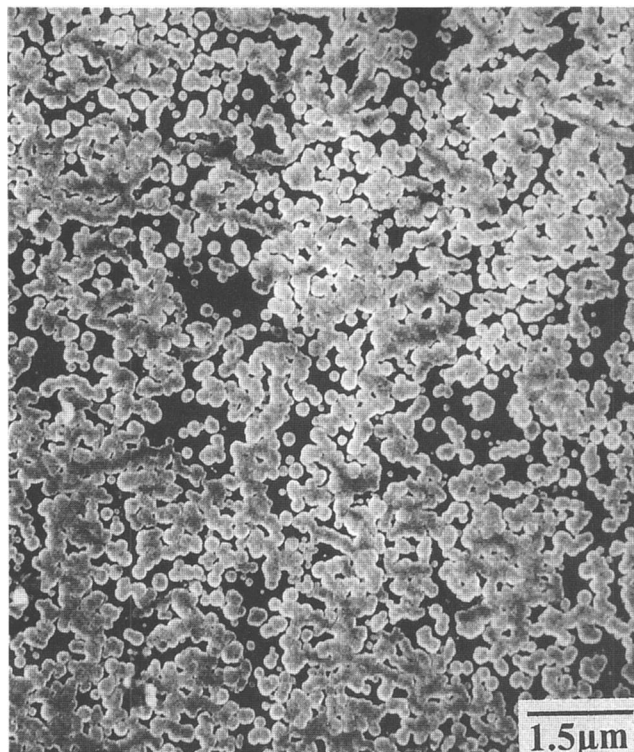

FIG. 1. SEM image of the sample after 5 min nucleation under 133 Pa.

although O$_2$ was applied to increase the growth rate. Many studies demonstrate that addition of oxygen increases the growth rate and lowers the possible growth temperature[16-19] by suppressing the formation of graphite carbon. Models have been advanced to explain the effects of O$_2$.[17] Usually, the substrate temperature is 700 °C–900 °C in HFCVD without the presence of oxygen. The growth rate decreases rapidly with a decrease in the substrate temperature and the filament temperature.[20] Therefore, it can be speculated that the growth rate would have been much lower than 0.26 μm if no oxygen had been used.

Figure 3 gives the Raman spectrum of the diamond film after 5 h growth, obtained in backscattering geometry with a spot size of 80 μm diameter. The strong peak at 1338 cm^{-1} is indicative of diamond. The slight shift of this peak away from 1332 cm^{-1} demonstrates compressive stress in the film. Meanwhile, there exists a broad peak centered at approximately 1530 cm^{-1}, which is attributed to amorphous carbon. However, it is very weak compared with the diamond peak. In combination with the good crystallinity of the film (Fig. 2), this demonstrates that the overall quality is considerably high. Howard et al.[21] reported oxygen poisoning in diamond, and thus decreasing intensity of the diamond peak in Raman spectra with the increasing addition of O$_2$. Therefore, the diamond peak would have been much stronger if oxygen had not been used under the same deposition parameters.
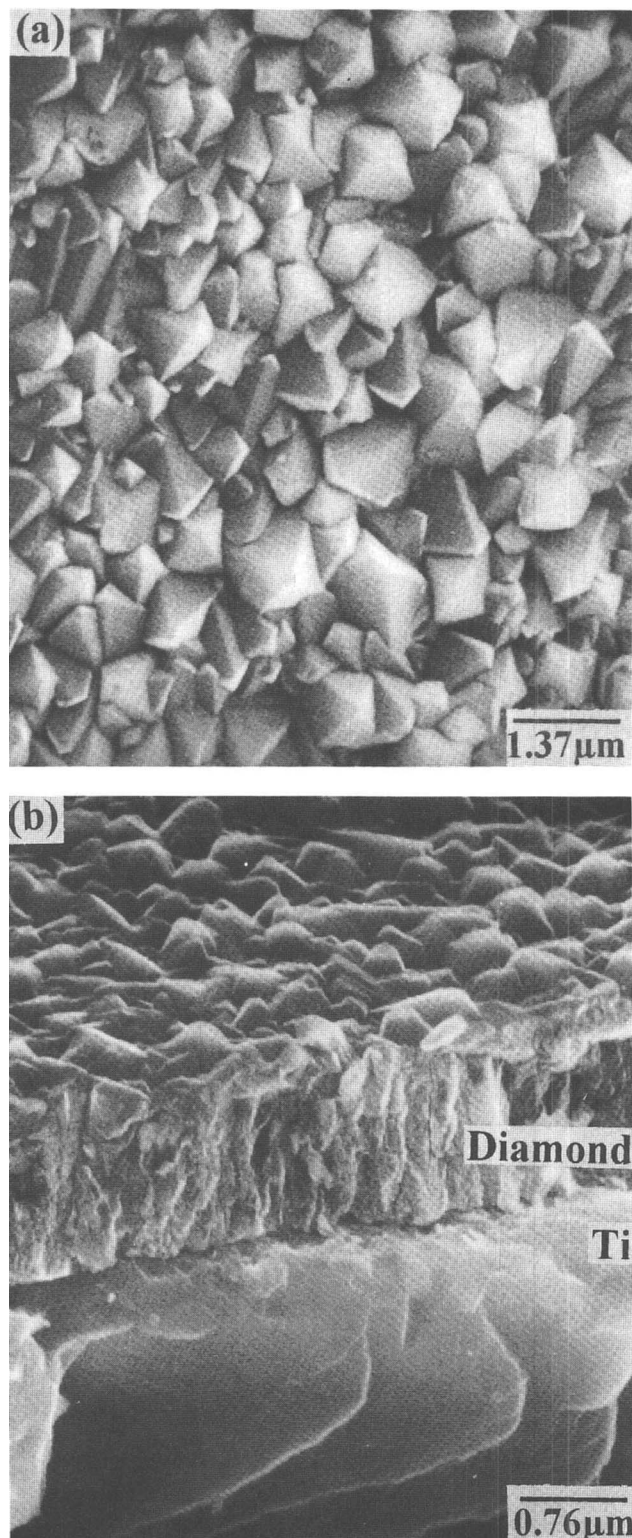
TABLE I. Detailed parameters in the experiment.

Parameters	Nucleation (step I)	Growth (step II)
Flow rate (sccm)	50	100
CH$_4$ concentration (vol %)	4.0	5.0
O$_2$ concentration (vol %)	0.0	0.4
Filament temperature (°C)	2100	1900
Substrate temperature (°C)	780	550
Pressure (Pa)	133	2660
Duration	5 min	5 h

FIG. 2. SEM micrograph of (a) the surface morphology and (b) cross section tilted at 75° of the as-grown diamond film after 5 h deposition.

FIG. 3. Raman spectrum of the diamond film.

In order to determine if there exists an intermediate TiC layer, x-ray diffraction was employed to analyze the as-grown film, as shown in Fig. 4. The peak indices are labeled in this figure. T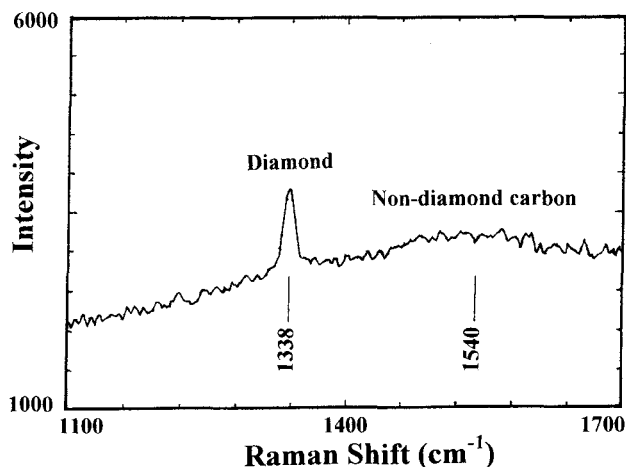he intensity ratio 0.36 of diamond (400) to diamond (111) is approximately 4.5 times greater than 0.08 for a powder, indicative of a (001) texture of the grown diamond film, in agreement with the SEM image in Fig. 2. No titanium hydride was detected by x-ray diffraction. However, peaks of 8F-TiC, though not intense, did appear, as shown in the figure. Therefore, we conclude that (i) the TiC interlayer is very thin, and that (ii) no detectable titanium hydride formed. This is ascribed to the rapid nucleation procedure as well as the relatively low growth temperature.

As of today, the mechanism of diamond nucleation on heterosubstrates is still not very clear. The formation of intermediate carbide layers usually precedes the nucleation process. It is critical to generate oversaturation of carbon atoms/radicals on the sample surface during nucleation. At high temperatures, the C atoms diffuse quickly into the substrate while atoms of the substrate also diffuse out to the surface, leading to the formation of carbide. If carbon is supersaturated on the sample surface, there still is a sufficient amount of hydrocarbon species to form graphite, amorphous carbon, or diamond particles, depending on experimental conditions. As soon as a continuous carbon layer forms, the diffusion and thus the formation of carbide are suppressed, followed by normal diamond nucleation and growth.

The very low pressure nucleation procedure is considered critical in our experiment. First, very low pressure greatly increased the mean free path of atomic hydrogen and hydrocarbon species and therefore the mass diffusivity. As a result, much larger amounts of atomic hydrogen and hydrocarbon species flowed onto the substrate surface from near the hot filament with little collision. Second, a large amount of electrons were emitted from the hot tungsten filament at very low pressure. This electron emission helped dissociate the hydrogen and hydrocarbons. These two factors caused oversaturation of hydrocarbon radicals on the Ti surface and led to rapid nucleation within a very short time (Fig. 1). Usually, the TiC interlayer is loose or porous,[15] unable
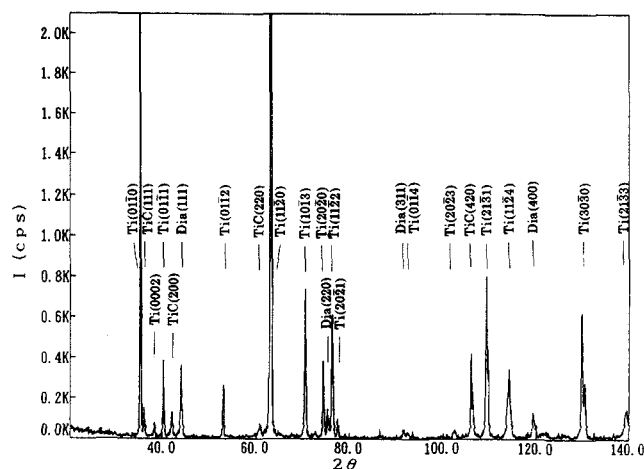
FIG. 4. The x-ray diffraction spectrum. Cu K_α was used as the source x-ray.

to prevent C atoms from diffusing into the Ti substrate; thus the diffusion of C atoms into the Ti substrate is very easy, much faster than into Si. Therefore, it is more important to generate oversaturation of hydrocarbon species on the surface of the Ti wafers. As shown in Fig. 1, high density nucleation was achieved within as short a time as 5 min. It can be speculated that such a high density of nuclei led to a continuous diamond film within a short time, and hence prevented the formation of TiC. As the nucleation duration was very short, the TiC interlayer was so thin as to be undetectable by SEM. In contrast, in Park et al.'s work,[15] the TiC interlayer grew up to 50 μm before the onset of nucleation. Moreover, they did not obtain continuous diamond film until after 4 h deposition. This can be attributed to the lack of oversaturation of hydrocarbon species for nucleation.

In addition, in order to build up the supersaturation of carbon, a much higher filament temperature (2100 °C), compared with that during the subsequent growth (1900 °C), was adopted because we had found that the nucleation rate was much lower when lower filament temperatures were used. This is attributable to the decrease of the ability of the filament to thermally decompose the reagent gases with decreasing temperature. Therefore, if a lower filament temperature had been used for nucleation, the amount of atomic hydrogen and reactive carbon radicals would have been much smaller and, therefore, the nucleation would have been much poorer. So we believe that a high temperature is also important for nucleation.

On the other hand, no titanium hydride was detected by x-ray analysis (Fig. 4). This demonstrates that hydrogenation of the Ti thin wafers proceeded very slowly at the low substrate temperature of 550 °C. The addition of O_2 to the source gases ensured that the diamond film still grew at such a low substrate temperature. Although the substrate temperature was much higher during the nucleation stage, the duration was very short, only 5 min, so little Ti hydride

formed. The thin titanium wafer retained its initial elasticity, and no serious hydrogen embrittlement occurred.

In summary, a very low pressure (133 Pa) and a high filament temperature were used to achieve high density nucleation within a short time (5 min), and accordingly, to suppress the formation of a TiC interlayer. Oxygen was added to source gases during the subsequent growth to enable diamond deposition at a considerable rate at a lower-than-normal substrate temperature (550 °C), and thus to slow down the hydrogenation speed of the Ti wafer. The combination of the very low pressure nucleation procedure and the addition of O_2 during subsequent deposition ensured that the Ti wafer retained its initial elasticity after deposition. Analyses demonstrate that little TiC formed and that no titanium hydride was detected.

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