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Quantitative characterization of the true epitaxial ratio in the first stage of the MPCVD diamond synthesis.

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Abstract

Isolated diamond crystals have been deposited on silicon by the microwave plasma assisted chemical vapor deposition technique (MPCVD) using the bias enhanced nucleation (BEN) step. The true epitaxial ratio, defined as the number of epitaxied crystals to the total crystal number before coalescence, has been calculated by high-resolution scanning electron microscopy coupled to image analysis software. This ratio is correlated to the conditions of the etching step which precedes the bias step. This investigation allows us to determine the better conditions to obtain homogeneous epitaxied deposit with an optimum epitaxial ratio in the absence of a preceding carburization step, and to propose a qualitative explanation about the effect of the etching step on the silicon substrate.

1. Introduction

Highly oriented diamond films deposited by chemical vapor deposition technique (CVD) have many excellent properties that are important for applications such as heat sinks, high temperature electronic devices and optical windows. More recent attention has focused on the processing of high quality diamond films in electronic applications. Therefore, the synthesis of heteroepitaxial diamond films on silicon substrates has been largely developed. As studied in previous papers [1,2], the main problem for this purpose is related to the difficulty to both increase and obtain a reproducible epitaxial ratio. This one rarely exceeds 10% when silicon is

used as the substrate. This value can be raised when a specific carburization step is carried out before the BEN step.

Some studies have emphasized that direct heteroepitaxy is achieved when the subsequent growth temperature is lowered and the bias-enhanced nucleation period is shortened [3,4]. Moreover, the quality of the diamond/silicon orientation (i.e. decreasing of the mosaicity) is improved when the biasing time and the voltage are reduced [1,5]. These results are in agreement with our previous results where an epitaxial ratio up to 6% can be achieved by using ultra short BEN step without carburization step [1,2]. In the conditions of these papers, we emphasized that the modification of the etching step conditions was a promising way to raise the epitaxial ratio and the nucleation density. A first approach highlighted that *ex situ* preparation of silicon substrates does not significantly affect the quality of epitaxy [6]. This behavior is probably linked to the substrate reoxidizing during the etching step in presence of residual oxygen inside the chamber. It is agreed by most researchers that the presence of a native oxide on silicon impedes the nucleation process. Stoner *et al.* [7] and Lee *et al.* [8] indicated that etching or biasing with pure hydrogen discharge does not permit the entire removal of SiO₂. This was confirmed by Pintér *et al.* [9] who observed that SiO₂ is partially removed after H₂ etching whereby the bias nucleation resulted in a mixture of SiO₂ and SiC. This residual oxide deposit is probably highly nonuniform as described in the case of SiO₂ decomposition under UHV conditions [10]. The presence of SiO₂ islands and hillocks [11] could explain the presence of non-oriented crystals near epitaxied ones although the bias discharge is homogeneous at this scale.

The density, the size and the thickness of these SiO₂ islands are thought to be very dependent on the etching step conditions preceding the bias. So, in this study, we modified these conditions and characterized the epitaxial ratio and the nucleation density after the subsequent bias and growth steps. Then, a continuous diamond film was synthesized from a deposit exhibiting the optimal epitaxial ratio.

2. Experimental

Deposition was carried out in a 2.45-GHz microwave plasma CVD reactor which has described in detail earlier [2,12]. The substrate/substrate-holder configuration was defined to optimize the microwave discharge and the extension of the bias discharge over the whole substrate surface [2]. To study the effect of the etching step, we added a ceramic tube that was positioned as illustrated in figure 1 and whose function is detailed through the next section. Square mirror-polished n-type Si(001) wafers (10x10x0.375 mm) were used as substrates in this investigation. These wafers were subsequently cleaned in acetone and rinsed in HF before placing them inside the reactor. The Si(001) substrate was preheated by the induction power supply under vacuum conditions ($P = 5 \times 10^{-4}$ Pa) for 150 sec. This heating step leads to the desorption of H-terminated passivated silicon and consequently to the formation of an oxide layer. This step also increases the substrate temperature, which is necessary to carry out the etching and nucleation steps. To precisely study the effect of the etching conditions, the bias-enhanced nucleation step was carried out at fixed conditions. For the epitaxial ratio determination, the growth time was limited to 30 min avoiding the coalescence step and for the diamond film synthesis, the growth time was fixed to 10 hrs. The experimental conditions are reported in Table 1.

The substrate temperature was measured in the range 834-1200 K by an optical pyrometer through a view port. We performed the quantitative characterization of the diamond deposits using a high-resolution scanning electron microscopy (HRSEM, Philips xl30s FEG) coupled with image analysis software (APHELION, ADCIS S.A.).

3. Results and discussion

3.1. Effect of hydrogen plasma power density

In order to modify the interaction between the plasma and the substrate (oxide layer), we modified the plasma power density by varying the hydrogen pressure during the etching steps. A first approach without the integration of the ceramic tube did not lead to a variation of the epitaxial ratio which remained approximately 6%. The introduction of the ceramic tube around the substrate-holder significantly increased the epitaxial ratio to about 16% for the same hydrogen pressure (10~13 hPa) [6]. Moreover, the modification of the ceramic material did not affect this ratio. It can be concluded that plasma volume modification thanks to the ceramic wall changed the plasma power density and improved the silicon oxide etching.

From this configuration, we studied the variation of hydrogen plasma power density as a function of hydrogen pressure during the etching step. The determination of the plasma power density was carried out by calculating the plasma volume as described by Grotjohn et al. [13]. As shown in figure 2, the plasma power density in a pure hydrogen discharge at 400 W absorbed microwave power was changed from 15.8 to 27.7 W/cm³ as the hydrogen pressure increased from 13 to 53 hPa which is consistent with the evolution reported by Grotjohn [13]. Figure 3 presents the results of the epitaxial ratio and the total nucleation density in relation to the plasma power density. We can show that the epitaxial ratio gradually increases when the plasma power density is raised to 25.1 W/cm³ (40 hPa), then seems to decrease for higher plasma power densities. So, the epitaxial ratio reached 26% ; this value is significantly higher than the classical ones reported in the literature (without a carburization step). We likewise show that the nucleation density evolved in the same manner with a maximum value for 25.1 W/cm³. Figures 4(a)~(c) show the high-resolution scanning electron micrographs of the isolated diamond crystals for three plasma power densities : 15.8 W/cm³, 25.1 W/cm³ and 27.7 W/cm³ respectively. HRSEM images of the samples show well-defined crystals with average grain size of about 200 nm. It can be seen in figure 3 that diamond nuclei were formed on the substrate with an average nucleation density of about $7.2 \times 10^9 \text{ cm}^{-2}$. The epitaxial crystals are visible and present a square (100) facet parallel to the (100) silicon. The

micrograph shown in figure 4b shows the very high epitaxial crystallite percentage (26 %) which were obtained for a plasma power density equal to 25.1 W/cm^3 . They are constituted by single or multiply twinned particles and are uniformly distributed on the whole substrate surface. The SEM micrograph reported in figure 4d shows the corresponding diamond film obtained for an epitaxial ratio equal to 26%. The film is about $4 \mu\text{m}$ thick and the surface morphology is representative of an evolutionary selection rule occurring during 9 hrs.

From these results, we can consider that the etching step followed by the bias step is necessary to induce diamond epitaxy. Indeed, the bias discharge without the preliminary etching step does not induce the nucleation of epitaxial crystals except for very long bias duration which is detrimental to the epitaxial quality (increasing in the mosaicity). For short bias duration, the etching conditions directly modify the epitaxial ratio probably by removing the silicon oxide present on silicon. If the etching discharge is not sufficiently efficient to remove this oxide, the bias discharge leads to the nucleation of epitaxial crystals only on areas free from the oxide. If the oxide removal is heterogeneous as expected in the introduction, epitaxied and randomly crystals can nucleate and grow near each other. If the etching step is very efficient, some oxide-free areas can suffer from the direct silicon etching, which probably leads to a local loss of the silicon structure (amorphization) [11,14]. Therefore we think that the efficiency of the bias is directly linked to its capacity to remove the residual SiO_2 which is not completely eliminated by the preceding steps. We cannot exclude the formation of silicon carbide during the BEN treatment but it is not sufficient to reach the present values of epitaxial ratio. The BEN step being performed at fixed conditions, the nature of the silicon carbide, if formed, is determined by the etching step. It is important to point out that the BEN step in our conditions (very short time and soft conditions) without the preceding step (etching step) did not induce diamond epitaxy. So the carbide formation during the bias is probably very weak and in any case not sufficient to induce epitaxy. The etching conditions must be chosen to obtain a good equilibrium between oxide removal and silicon

structure disturbance. The evolution of the epitaxial ratio in relation to the plasma power density during the etching step seems to be representative of this equilibrium. This study is in progress to still increase the quality of the diamond/silicon epitaxy.

4. Conclusion

The epitaxial ratio and the total nucleation density can be affected by varying plasma power density as a function of the hydrogen pressure during a H₂ etching step preceding bias-enhanced nucleation. We obtained 26% epitaxial diamond crystals for total crystal densities above $1.0 \times 10^9 \text{ cm}^{-2}$ without specific carburization step and for a low bias step duration. The etching conditions must be chosen to obtain a good equilibrium between oxide removal and silicon structure disturbance.

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