

Investigation of the {100}-oriented texture growth of diamond film as functions of carburization and bias enhanced nucleation times

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The {100}-oriented texture growth of diamond films on {100} Si substrate ($1 \times 1 \text{ cm}^2$) could be achieved by a three-step procedure (carburization $\rightarrow$ bias enhanced nucleation (BEN) $\rightarrow$ growth) in a microwave-plasma-enhanced chemical vapor deposition (MPECVD) system. The surface morphologies of the films were investigated as functions of the carburization and BEN times. We demonstrated the necessity of the carburization step of at least 100 minutes to readily achieve the textured growth of a diamond film. The grain size increased with increasing carburization time or BEN time. We studied the effects of the carburization time and the BEN time on the {100}-oriented texture growth of a diamond film. The optimal BEN time was suggested by considering the carburization time. The evolution of the film morphology indicates that the increase in carburization time may decrease the tilted angle of the {100}-oriented texture morphology.

Key words: {100}-Oriented texture growth, Diamond film, Carburization, BEN.

Introduction

Recently, the {100}-oriented texture growth of diamond film has received more attention than ever because {100}-oriented grains are known to have a much smoother surface than grains of other orientations [1, 2]. Therefore, this morphology has been accepted as an optimal diamond surface to fabricate diamond electronic device [3, 4].

To obtain the {100}-oriented texture growth, a three-step procedure (carburization $\rightarrow$ bias enhanced nucleation (BEN) $\rightarrow$ growth), a conventional method, has been introduced [3]. A carburization step was introduced to assist the formation of the diamond nuclei. The carburization technique uses the decomposition reaction of a hydrocarbon gas prior to the nucleation step. Therefore, it can produce a great deal of carbon species during the carburization reaction. This method may enhance diamond nucleation during the initial nucleation stage. The BEN step was originally developed to enhance the nucleation of a diamond film without using the diamond scratch pretreatment on a Si substrate [5]. Since the BEN technique uses a direct application of negative bias voltage on Si substrate, the state

of the diamond film may be strongly affected by the state of the Si substrate. Therefore, it was possible to obtain {100}-oriented texture morphology of diamond films by applying a BEN step on the {100} Si substrate during the nucleation stage.

Unfortunately, the lattice mismatch between diamond ($a = 35.7 \text{ nm}$) and silicon ($a = 54.3 \text{ nm}$) is too large (52 %) [6]. Therefore the adhesion will be worse and the texture morphology induced by a Si substrate will be reduced. One of the methods to reduce the lattice mismatch is to put on an interlayer between the diamond film and the Si substrate. β -SiC ($a = 43.6 \text{ nm}$) is a promising method for this purpose, as it has a relatively small lattice mismatch (22%), compared with that (52 %) of a Si substrate [6, 7]. A β -SiC interlayer is usually formed during a BEN step [8]. The carburization step was also found to form a β -SiC interlayer between the film and the substrate [9].

Despite the intensive research in the {100}-oriented texture growth of diamond films, detailed studies regarding the effect of the carburization and BEN times are few. The purpose of our work is to investigate the effect of the carburization and BEN times on the {100}-oriented texture growth of diamond film. After each step, the detailed surface morphologies and film characteristics were investigated. Based on these results, we determined the optimal application time for each step and discussed the effect of the carburization and the BEN steps.

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Experimental

Diamond films were deposited on n-type Si {100} substrates in a microwave-plasma-enhanced chemical vapor deposition (MPECVD) system. Prior to the film deposition, the substrates ($1 \times 1 \text{ cm}^2$) were cleaned using H_2 plasma in a MPECVD system. The cleaning was carried out at a microwave power of 900 W, a substrate temperature of 800°C , and a total pressure of 20 Torr in a static MPECVD system. For film deposition, 2% CH_4 and 98% H_2 gases were used as source gases at a total flow rate of 200 sccm. The deposition parameters were 1000 W, 700°C , and 25 Torr, throughout the carburization $\rightarrow$ BEN $\rightarrow$ growth step.

Many parameters must be optimized to achieve a dense and oriented film. The bias voltage is one of the most important parameters. In our gas composition, the negative bias voltage, used in the BEN step, was applied at between -200 V and -250 V . We investigated three bias voltages, and set the optimal bias voltage at -220 V for this work.

The position on the sample is another main parameter. There has been a great deal of interest in this parameter in recent reports [10, 11]. All measurements in this work were carried out as a function of the position on the sample. For the substrate, we immersed the substrate into the plasma during the BEN step. For

all other steps, we placed the substrate at the bottom of the plasma. The morphologies of film surfaces were examined using optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). The qualities of the diamond films were investigated by Raman spectroscopy.

Results and Discussion

In our first investigation, a bias voltage to achieve both a good nucleation density and satisfying morphology in the BEN step was applied. After 150 minutes of carburization $\rightarrow$ 10 minutes of BEN $\rightarrow$ 900 minutes of the growth step using different bias voltages, we investigated the film morphologies as a function of the applied bias voltage (-200 V , -220 V , and -240 V) in the BEN step.

Figure 1 shows the film surface morphologies examined by AFM as functions of the different positions on the sample and the applied bias voltages. Figs. 2a~c show the shape of one of the grains in Fig. 1, whose sizes are roughly 4.0 nm . At -200 V , a hexagonal grain shape can be observed (Fig. 2a). At the same time, no film formation was observed on the Si substrate (see Figs. 1a~c). This hexagonal shape suggested the presence of hexagonal diamonds such as lonsdaleite or polytypes. By increasing the negative bias voltage, the grain takes

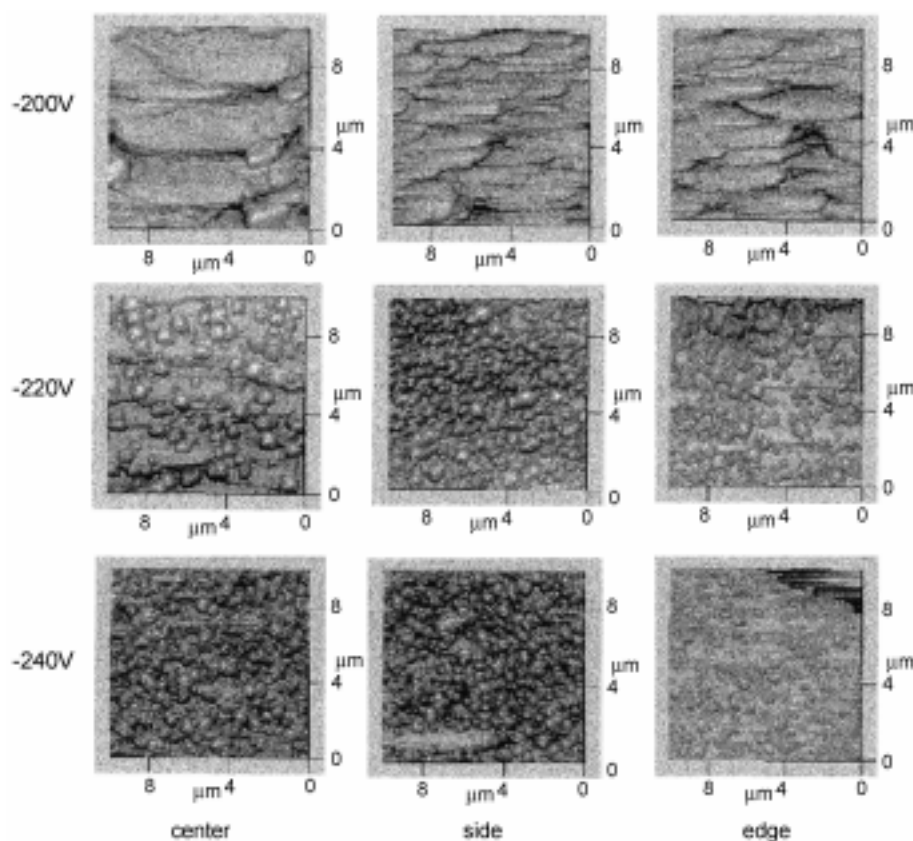


Fig. 1. AFM images of the film surface after 150 minutes carburization $\rightarrow$ 10 minutes BEN $\rightarrow$ 900 minutes growth step as functions of the applied bias voltage and the position on the sample.

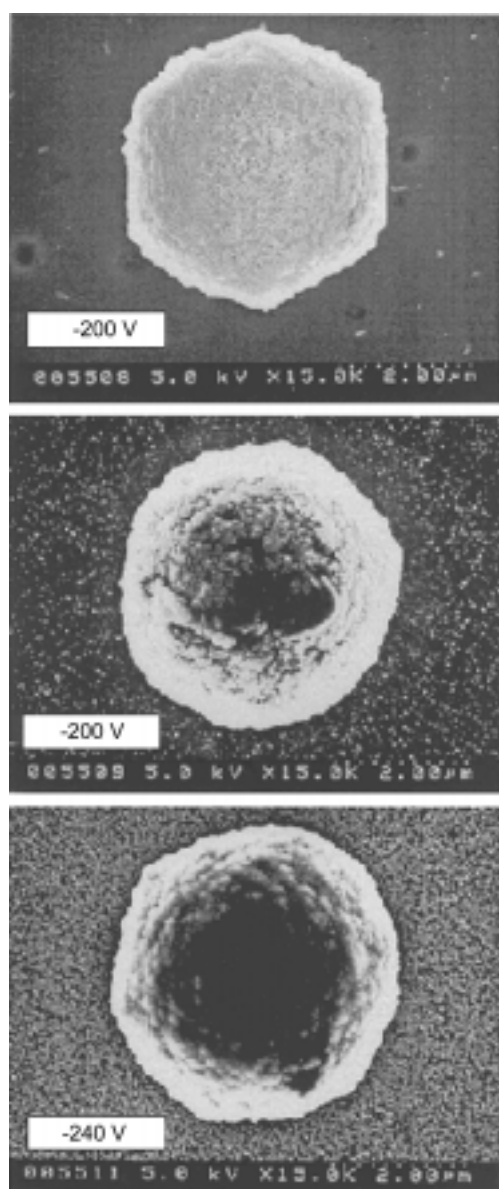


Fig. 2. SEM images of the grains after 150 minutes carburization → 10 minutes BEN → 900 minutes growth step as a function of the applied bias voltage.

on a more ball-like shape, as shown in Figs. 2b and c, indicating deterioration of the crystallization. This demonstrates that there may be a decrease in the diamond quality of the grain by increasing the negative bias voltage. The reason for this may be as follows: it has already been demonstrated that the induced current on the substrate decreases with increasing the negative bias voltage. Furthermore, there is an increase in the CH_4 concentration [12]. We assume that an increase in the negative bias voltage may be related to an increase in the CH_4 concentration. Consequently, increasing the negative bias voltage, as increasing the CH_4 concentration, may deteriorate the formation of a diamond grain. Fig. 1 also shows the increase in the nucleation density with increasing the negative bias voltage,

indicating better stabilization of the nuclei. This is in accordance with other reports on nucleation density as a function of the applied negative bias voltage [13]. Furthermore, we observed that the diamond grains show a better orientation at -220 V, concerning the $\{100\}$ -oriented texture morphology at -220 V (see Figs. 1d~f). This finding concurs with the fact that a critical bias voltage is necessary to obtain the $\{100\}$ -oriented texture morphology.

In the next step, the bias voltage at -220 V was set and a systematic study was made, using different times for the carburization step. For the investigation of the optimal carburization time, we prepared four samples whose carburization times were 0, 10, 100, and 150 minutes. After 30 minutes for the BEN step of each sample, the diamond grain quality was analyzed using the micro-Raman spectroscopy, equipped with a He-Ne laser source. The results shown in Fig. 3 are the functions of the carburization time and the position on the sample. The spectra shows four peaks, which are the D band around 1350 cm^{-1} , the G band of microcrystalline graphite around 1590 cm^{-1} , and two small peaks from SiC at 796 and 947 cm^{-1} [14]. The position of the peak at 796 cm^{-1} is in accordance with the literature [14, 15], but the last peak at 947 cm^{-1} has a different Raman shift from that usually found. Such important Raman shifts have already been explained by the effect of the treatment by SiC [15]. At the center position on the samples, the SiC peaks show a reduced intensity, whereas the microcrystalline graphite peaks increase with increasing carburization time. Because the microcrystalline graphite was mainly composed of carbon species, we may consider that the carbon species in the grain increases gradually with increasing carburization time. Above 100 minutes, we observed the saturation of an increase in the peaks with increasing carburization time (see Figs. 3e~h). These results reveal that at least of 100 minutes of the carburization step is necessary to obtain the fully carbon, instead of SiC, incorporation in the grain as a microcrystalline graphite form.

The effect of BEN times was tested using the micro-Raman spectra. Our findings show that by increasing the BEN time there was an increase in the D and G bands peaks corresponding to microcrystalline graphite, as shown in Fig. 4. This result also indicates an increase in microcrystalline graphite incorporation in the grain with increasing BEN time.

Images of the edge position on the samples after the carburization → BEN step were examined as functions of carburization time and BEN time as shown in Fig. 5. It clearly shows that the nucleation density is affected by both the carburization time and the BEN time. Increasing the BEN time results in increasing the nucleation density on the edge position on the samples. It also increases the nucleation density of the large grains (the diameter $> 4\text{ }\mu\text{m}$), which are an obstacle in

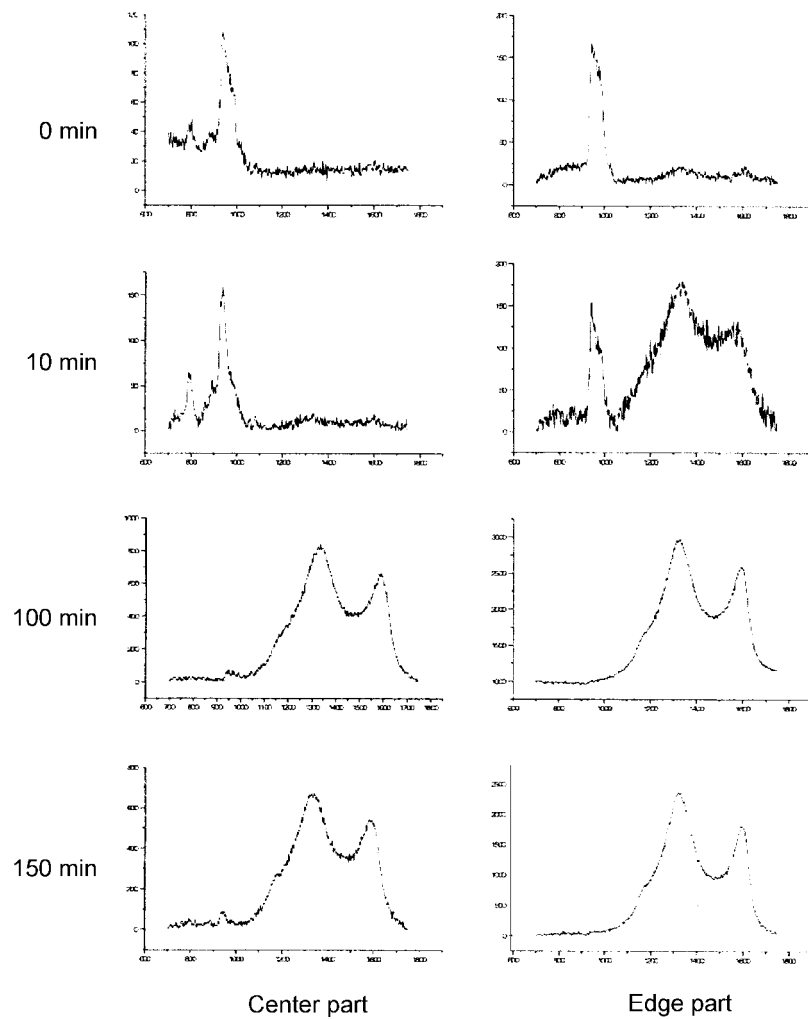


Fig. 3. Micro-Raman spectra of the grains after carburization step as functions of the carburization time and the position on the sample.

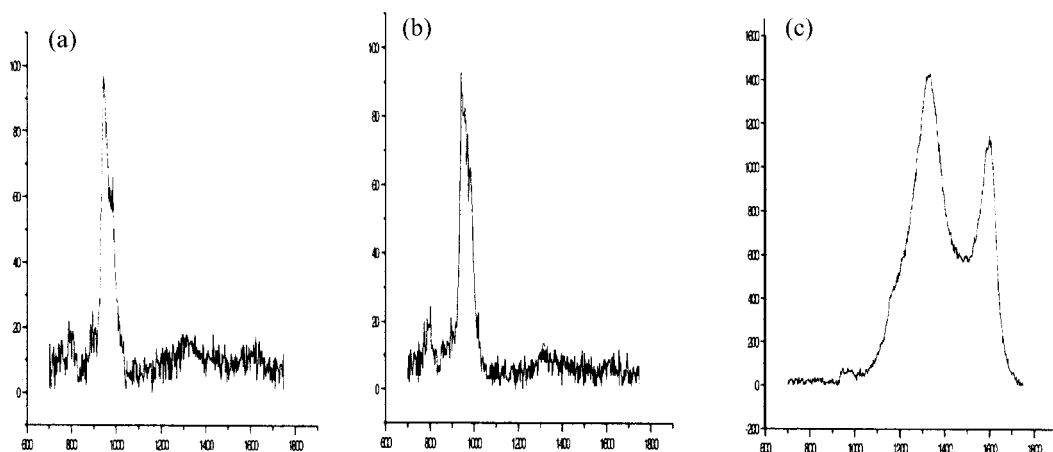


Fig. 4. Micro-Raman spectra of the grains after 100 minutes carburization → BEN step as a function of BEN time. BEN times are (a) 5, (b) 10, and (c) 30 minutes, respectively.

the electronic device application of diamond films.

We investigated the detailed surface morphologies of these samples using AFM as shown in Fig. 6. On the whole, we found a well-developed {100}-oriented texture

morphology for a longer carburization time (150 minutes). In this case, the size of the textured grain increases with increasing BEN time. At 30 minutes of BEN, we also found the increase of the grain size with

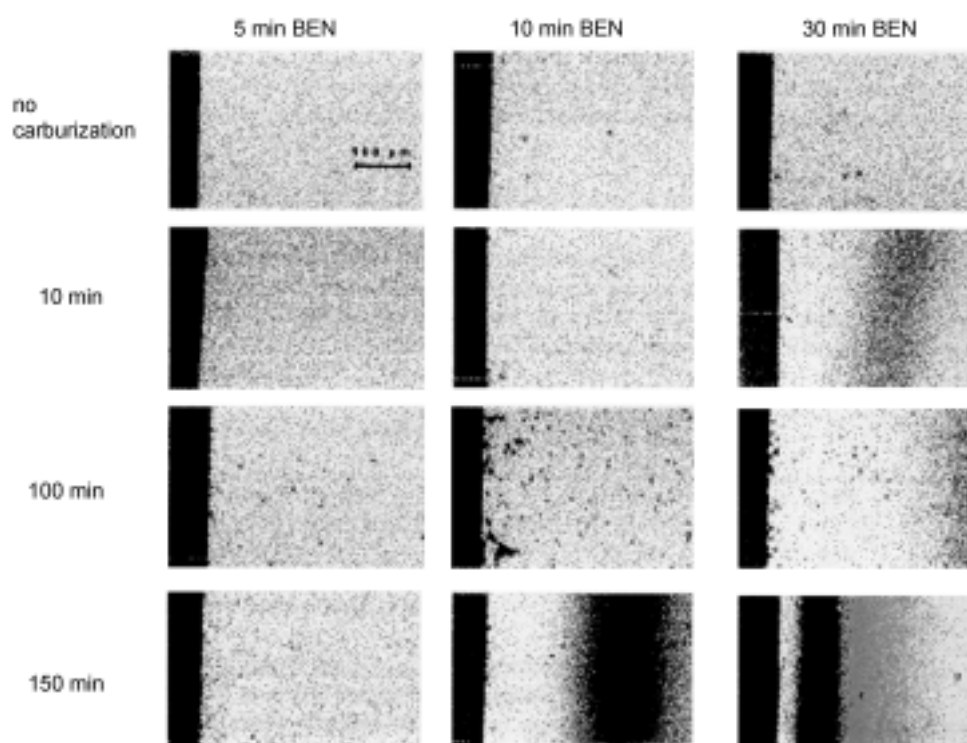


Fig. 5. Optical microscope images of the edge position on the samples after carburization → BEN step as functions of the carburization and BEN times.

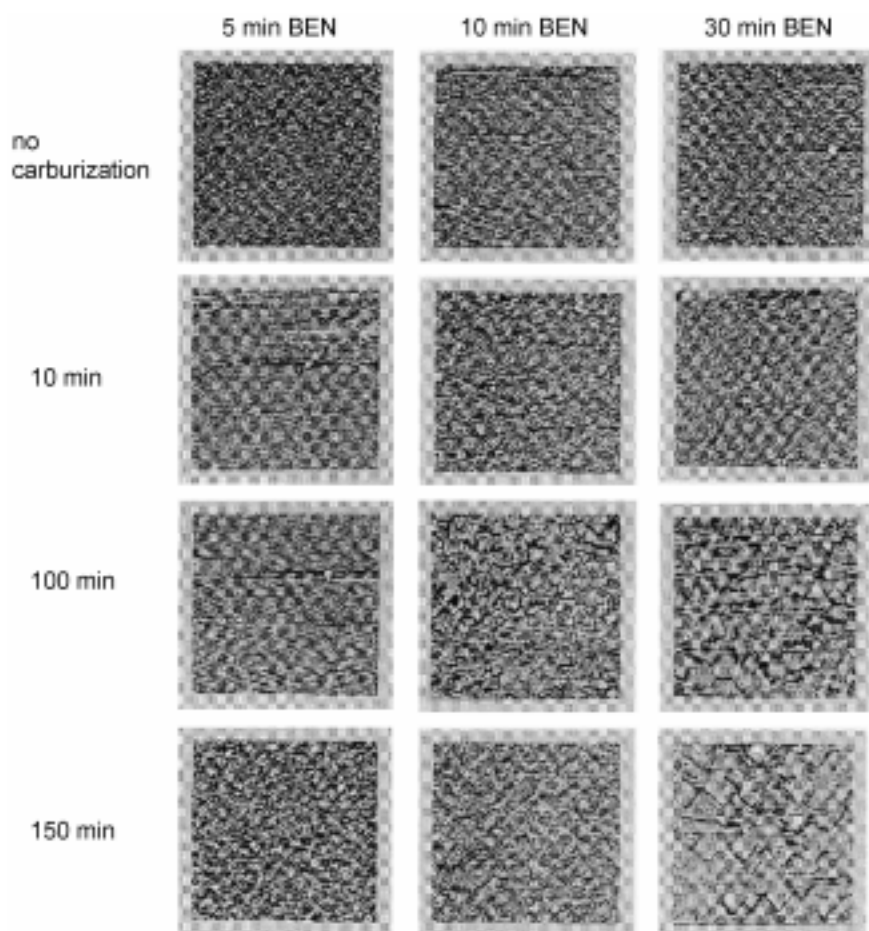


Fig. 6. AFM images of the edge position on the samples as functions of the carburization and BEN times.

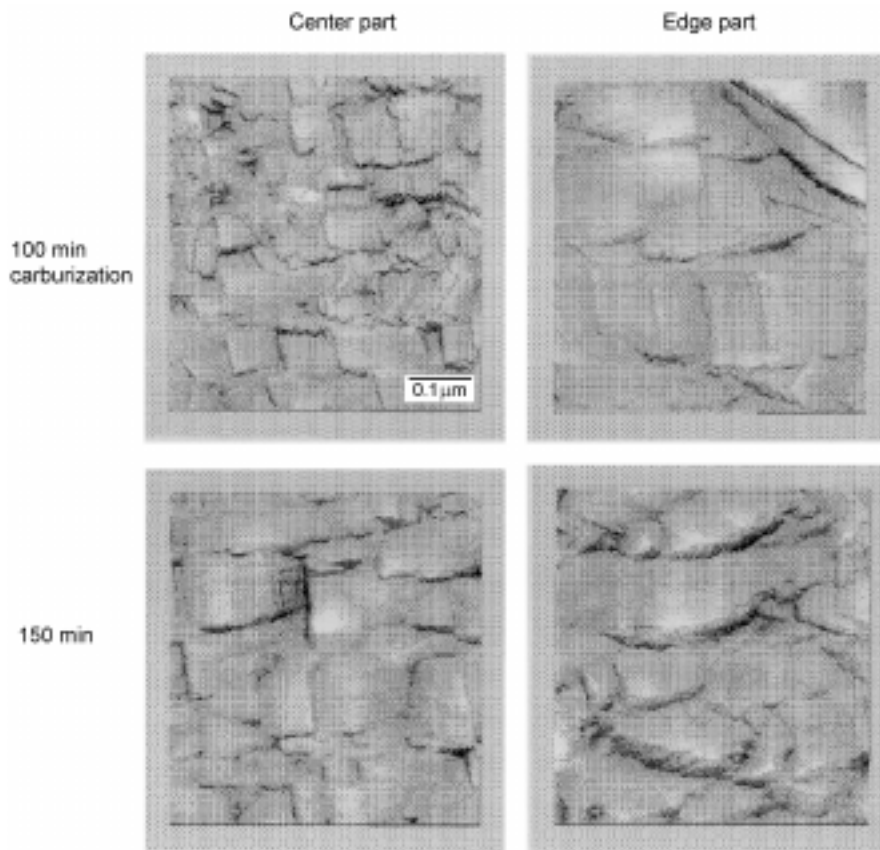


Fig. 7. AFM images of the samples after carburization → 10 minutes BEN → 18 hours growth step as functions of the carburization time and the position on the sample.

increasing carburization time. Obviously, these results reveal that there is a correlation between the grain size and both the carburization and BEN time. Based on these results, we suggest that BEN time should be optimized according to carburization time. In addition, we observed a 45° tilted orientation of the {100}-oriented grain, compared with a {100} Si substrate.

After 100 or 150 minutes of the carburization → 10 minutes BEN → 18 hours growth step, we investigated the evolution of film morphology as a function of the positions on the sample as shown in Fig. 7. According to the morphologies of the position on the sample, the results are different before and after each growth step. Before the growth step, the deposition of nano-crystals was mainly on the edge position, whereas after the growth step they were mainly on the center position with a well-developed {100}-oriented texture morphology. The {100}-oriented texture morphology was tilted at about 20° on the 100 minutes carburized sample, whereas it was tilted at 9.7° on the 150 minutes sample. This result strongly indicates that the increase in the carburization time decreases the tilt angle.

Conclusions

We investigated the carburization and BEN steps. The morphology of the deposited films appears to be

highly dependent on the times of the carburization and BEN application. We demonstrated the necessity of the carburization step for at least 100 minutes to obtain a fully carbonized grain. We found that there is a correlation between the grain size and both the carburization and BEN time. After the BEN step, we observed the {100}-oriented texture morphology which showed a tilted angle of $\sim 45^\circ$. After the growth step, we found a decrease in the tilted angle with increasing carburization time.

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