Research Article

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Evolution of surface morphology and properties of diamond films by hydrogen plasma etching

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Abstract: The micron-scale diamond film was prepared using hydrogen and methane as the mixed gas supplies via self-developed 3 kW/2,450 MHz microwave plasma chemical vapor deposition (MPCVD) equipment. On this basis, the evolution of the surface morphology, hydrophobicity, and electrical properties of samples under different hydrogen plasma etching times was investigated. The results indicate that the crystal edge and the top of the diamond grain were preferentially etched when etching time is less than 30 min. The surface roughness reduced from 0.217 to 0.205 μm, and the resistance value decreases from 3.17 to 0.35 MΩ. However, as the etch time increases to 120 min, the etching depth increases, and the surface roughness was increased. Simultaneously, the contact angles increased from 62.8° to 95.9°, which indicates that the surface of the diamond films exhibits more pronounced hydrophobicity. The treatment time of hydrogen plasma has no significant effect on the resistance value in the range of 0.26–0.50 MΩ. The mechanism of surface etching by hydrogen plasma was also discussed.

Keywords: microwave plasma chemical vapor deposition, diamond film, surface treatment, hydrogen plasma

1 Introduction

The diamond is a crystalline material composed of a carbon atom. It belongs to the equiaxial crystal system, and the crystal structure is face-centered cubic. Diamond's unique crystal structure determines its excellent physical and chemical properties [1]. Since natural diamonds come in a wide variety of shapes, it is not easy to apply them in practical applications. The excellent properties of chemical vapor deposition (CVD) diamond films are similar to natural diamond such as high thermal conductivity, high stability, and superhardness. Therefore, the CVD diamond has been studied widely in recent years [2–4]. With the further development of diamond technology in the field of optics, electricity, and acoustics, the requirements for surface morphology and flatness control will be more stringent [5–7]. In addition to surface flatness and damage control techniques [8], the diamond surface bond state also determines its practical application. At the same time, surface wettability is directly related to the application area of diamond film. For example, biological cells require hydrophilic surfaces for adhesion and growth; conversely, diamond coatings used to protect equipment from chemical attacks require hydrophobic films [9]. Moreover, if the high resistance problem of the diamond film can be improved, it can also be better developed in the semiconductor field.

Currently, mechanical polishing and plasma treatment techniques are mainly used to control the diamond surface. The mechanical polishing process is inefficient and prone to processing damage [10]. Up to now, plasma etching is the primary and most effective method for diamond surface morphology and bond state modulation. Plasma etching technique is to precisely control the sample by sputtering, reactive ions, high-density plasma, etc., in the presence of ions. The advantages of this method are fast reaction rate, low pollution, readily adjustable auxiliary gas, and process parameters. However, this method also has certain disadvantages, such as preferential etching of grain boundaries of diamond films, plasma etching rate is slow, and etched surface flatness is difficult to control, etc. [11]. The diamond can

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form a carbon–hydrogen bonding state on the surface after hydrogen plasma treatment. This bond state enables the diamond with a p-type conductive. Studies show that diamond surface carbon–hydrogen bonding state has high conductivity, stability, and corresponding device performance [12–19]. However, the surface of a diamond becomes rough due to excessive plasma etching time in the hydrogen terminal formation process, which severely affects the performance of hydrogen terminal diamond and its related electronic devices. As a result, controlling the flatness of the diamond surface and the carbon–hydrogen bonding state is particularly important for hydrogen terminal diamond applications.

In this article, the effect of different hydrogen plasma etching times on the micron-scale diamond film is studied. The surface morphology and roughness of diamond films are characterized by a scanning electron microscope (SEM) and an atomic force microscope (AFM). The effect of hydrogen plasma etching on the wettability of diamond surface is investigated by angle contact measuring device. Finally, the effects of etching on the diamond surface conductivity are characterized by four-probe resistance tester.

2 Experimental section

2.1 Preparation of high-quality micron-scale diamond film

The single-sided polished silicon wafer (2.54 cm × 2.54 cm, 100-oriented, p-type) was used as a starting substrate. Before the preparation of diamond, the silicon substrate was first mechanically polished and sonicated. The surface of the substrate creates a uniform scratch by pretreatment. These scratches will provide growth spots for polycrystalline diamond growth. Pretreatment can not only shorten the nucleation time but also effectively improve the nucleation density of diamond film [20]. The first step of diamond

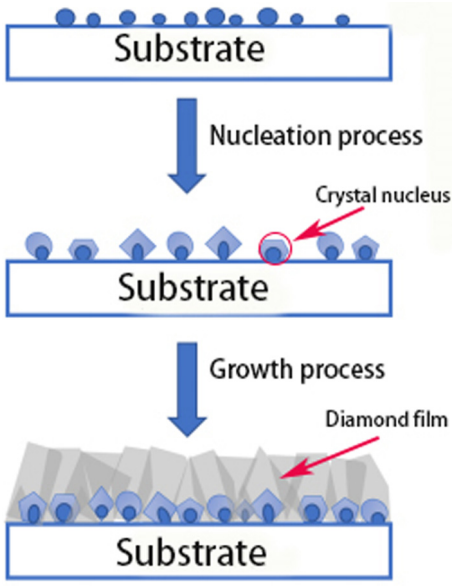

Figure 1: Schematic diagram of diamond grain growth.

growth is the nucleation process, which directly affects the quality of diamond. Therefore, in addition to substrate type and pretreatment method, nucleation parameters are also very important. Adopt self-developed 3 kW/2,450 MHz microwave plasma chemical vapor deposition (MPCVD) device. The nucleation was performed for 1 h with a microwave power of 1,700 W, a hydrogen flow rate of 400 sccm, a methane flow rate of 12 sccm, a gas pressure of 12 kPa, and a temperature of 700°C.

Diamond nucleation lays a good foundation for the subsequent growth of high-quality diamond film, while the growth of diamond film is more important. Figure 1 shows the process of the growth of polycrystalline diamond, the grains gradually grow up and contact with each other, and grains were changed from transverse to longitudinal growth [21]. The growth parameters are as follows: microwave power is 2,200 W, methane/hydrogen ratio is 2.4%, gas pressure is 14 kPa, and diamond is grown at 850°C for 4 h. The thickness of the grown micron diamond film is about 6–10 μm.

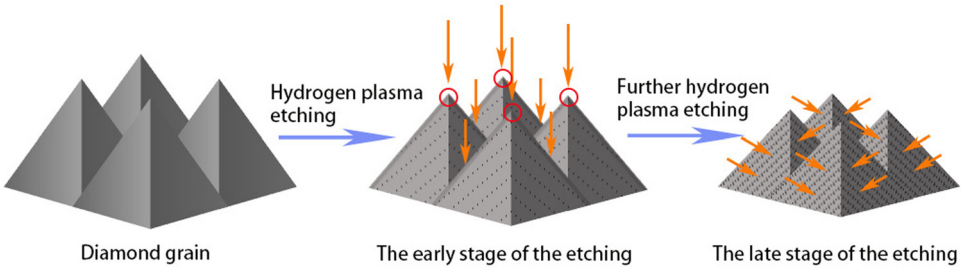

Figure 2: Plasma etching diamond film flattening process schematic.

2.2 Hydrogen plasma etching

The surface of the micron-scale diamond film has a certain roughness. Diamond films were etched with hydrogen plasma to make the (111) orientation surface flat [22,23], and Figure 2 shows the planarization schematic. The diamond films were treated with hydrogen plasma. Etching is performed in an MPCVD apparatus. The following parameters were utilized for etching: a microwave power of 2,000 W, a hydrogen flow rate of 200 sccm, a gas pressure of 10 kPa, and a temperature of 700°C. Five bunches of etching tests beneath diverse time were carried out. The etching time is 0, 30, 60, 90, and 120 min, respectively.

3 Results and discussion

3.1 Surface morphology

SEM of the prepared diamond films is shown in Figure 3. The micron-sized diamond films were prepared under the aforementioned process conditions: fast growth rate, good homogeneity, and high quality. It has a typical octahedral morphology and grain (111) preferred orientation. It demonstrates that the crystalline grains that have formed on the surface of the diamond are compact and homogeneous. The growth rate is about 1.706 $\mu m \cdot h^{-1}$, and purity of the diamond phase is about 85.7% [24].

The SEM images of the diamond films before and after etching are displayed in Figure 4. The crystalline grain of the initial CVD diamond films had no visible flaws. The crystalline grains are complete and uniform (Figure 4a). After 30 min of etching, the crystalline surface has a significant number of pits and steps (Figure 4b). The grain edges become blurry, and the grain boundaries became more evident. This kind of phenomenon can be due to adjacent position, which was more susceptible to etching. The diamond big grains collapse into tiny grains, and the graphite phase is etched by hydrogen plasma at the grain boundaries. Figure 4c shows that as the etching duration increases to 60 min, the number of etched pits on diamond grain surface increases and grain boundary deepens, the grain outline becomes more blurred, and the grain edges are more seriously etched than at 30 min of etching. When the etching time is prolonged further, the etching speed of the border of the grain increases significantly. Simultaneously, the edge of the crystal's etching is deeper, as shown in Figure 4d. When the etching time is up to 120 min, the etching is more severe at the grain boundaries, and the grain collapse tends to be flat (Figure 4e).

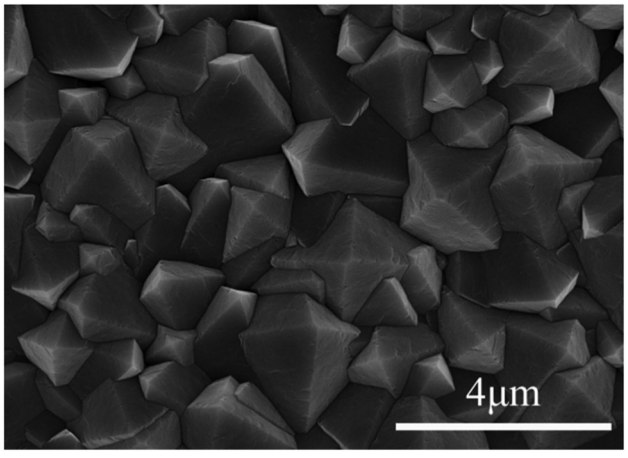

Figure 3: SEM morphology of micron-scale diamond film surface.

Electrons are known to be easily emitted from the crystal edge. The electric field increases as the number of electrons at the crystal edge rises. Therefore, the ions are not attracted to bombard the edge of the crystal because the moving electrons are suppressed to the surface of the film [25,26]. As a consequence, the crystal edge and top of the grain are preferentially etched during the early stages of hydrogen plasma treatment [27]. The non-diamond phases at the diamond grains and grain boundaries are etched by hydrogen plasma, and the depth of grain boundaries increases significantly. At this point, it is also fastest collapse of the diamond grains. Etching becomes more concentrated on the grain boundary as the etching duration increases. Although the degree of edge etching is still increasing significantly and further collapse of grains has occurred, the morphological changes at this point are less than those at the early stage of the etching. This is due to the hydrogen plasma's etching rate on graphite phase, which is approximately 50 times higher than that on diamond phases. So, graphite phase in the early stage of the etching was removed. The formation of CH and C_2 groups during etching proves that hydrogen plasma interacts with C atoms on the diamond surface. The reaction kinetics during etching proved faster etching at diamond defects [28].

3.2 Surface roughness

As is shown in Figure 5, when the etching time is 0, 30, 60, 90, and 120 min, the surface roughness of the samples in the 8 μm × 8 μm test range is 0.217, 0.205, 0.239, 0.256, and 0.316 μm, respectively. Therefore, the roughness of

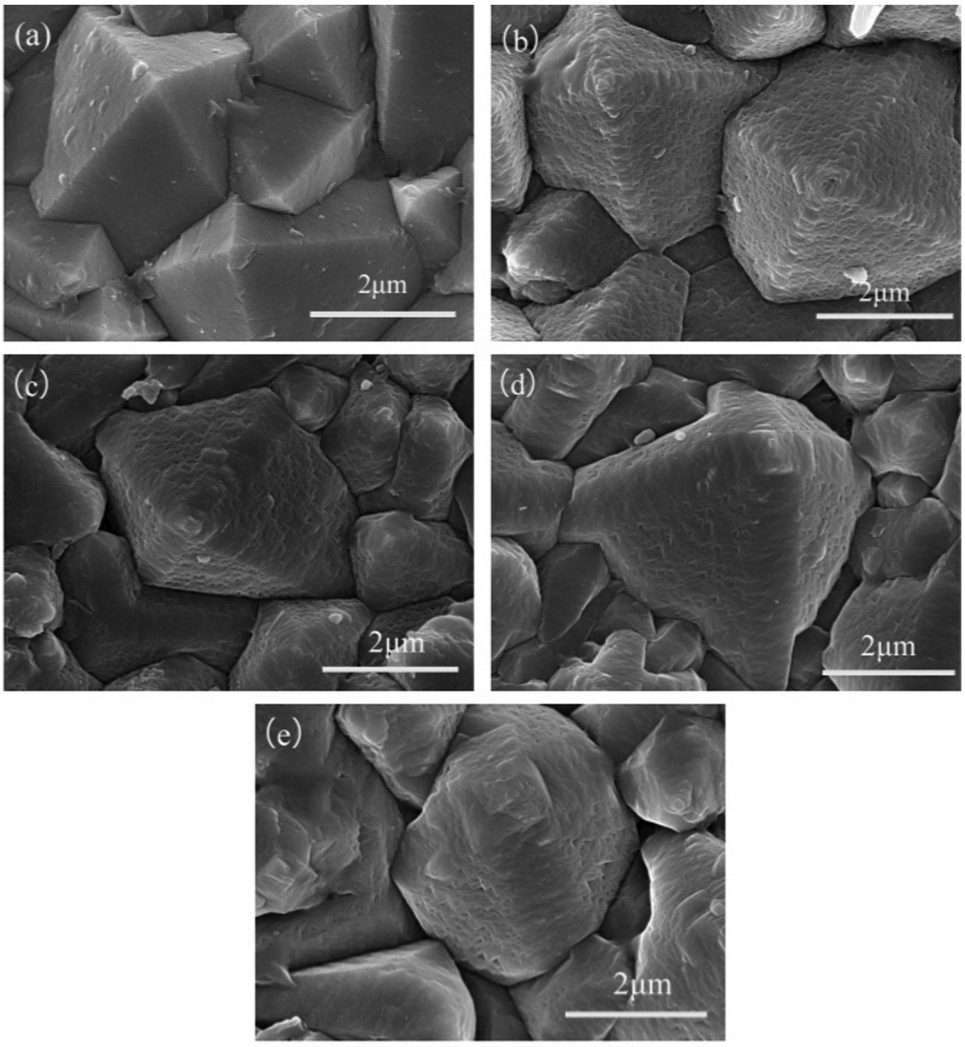

Figure 4: SEM images of samples etched at various times: (a) 0, (b) 30 min, (c) 60 min, (d) 90 min, and (e) 120 min.

the original micron diamond film is 0.217 μm (Figure 5a). After 30 min of hydrogen plasma etching, the roughness is reduced to 0.205 μm (Figure 5b). The diamond grain edges and top are severely etched. With the grain collapse into small island-shaped grains, the crystalline grains flatten somewhat. The etching speed of the top of the grain and the edge of the crystal is faster than the etching speed of the grain boundary, and it is preferentially etched in steps along the surface of the grain. Therefore, the change in grain etching effect results in the lowest surface roughness at this time. When the etching time further extends to 60 min, surface roughness of the sample is increased to 0.239 μm (Figure 5c). Although the grain boundary continues to deepen, the collapse rate of diamond grains is much lower than that in the early etching stage. With the prolongation of etching time, there is an increase in the number of etching pits. Therefore, the surface roughness of samples has increased. When the etching time is extended 90 min, increase of etching pits on diamond surface and increase of step-like pits on grain edges. At the same time, the grain boundaries continue to deepen. The roughness increases to 0.256 μm (Figure 5d). When the etching time reaches 120 min, the largest roughness of the sample is about 0.316 μm (Figure 5e). The later stages of etching mainly show an increase in the number of craters on the grain surface, a continuous deepening of grain boundary etching, and an increase in the degree of step-like etching on the grain edges. The etching forms etching pits at defects such as dislocations, and the anisotropic effect of grain etching also comes out gradually.

The relationship between sample roughness and etching time shows that plasma etching increases the surface roughness of the sample. As the etching time increases, the surface roughness decreases from 0.217 μm at first to 0.205 μm and

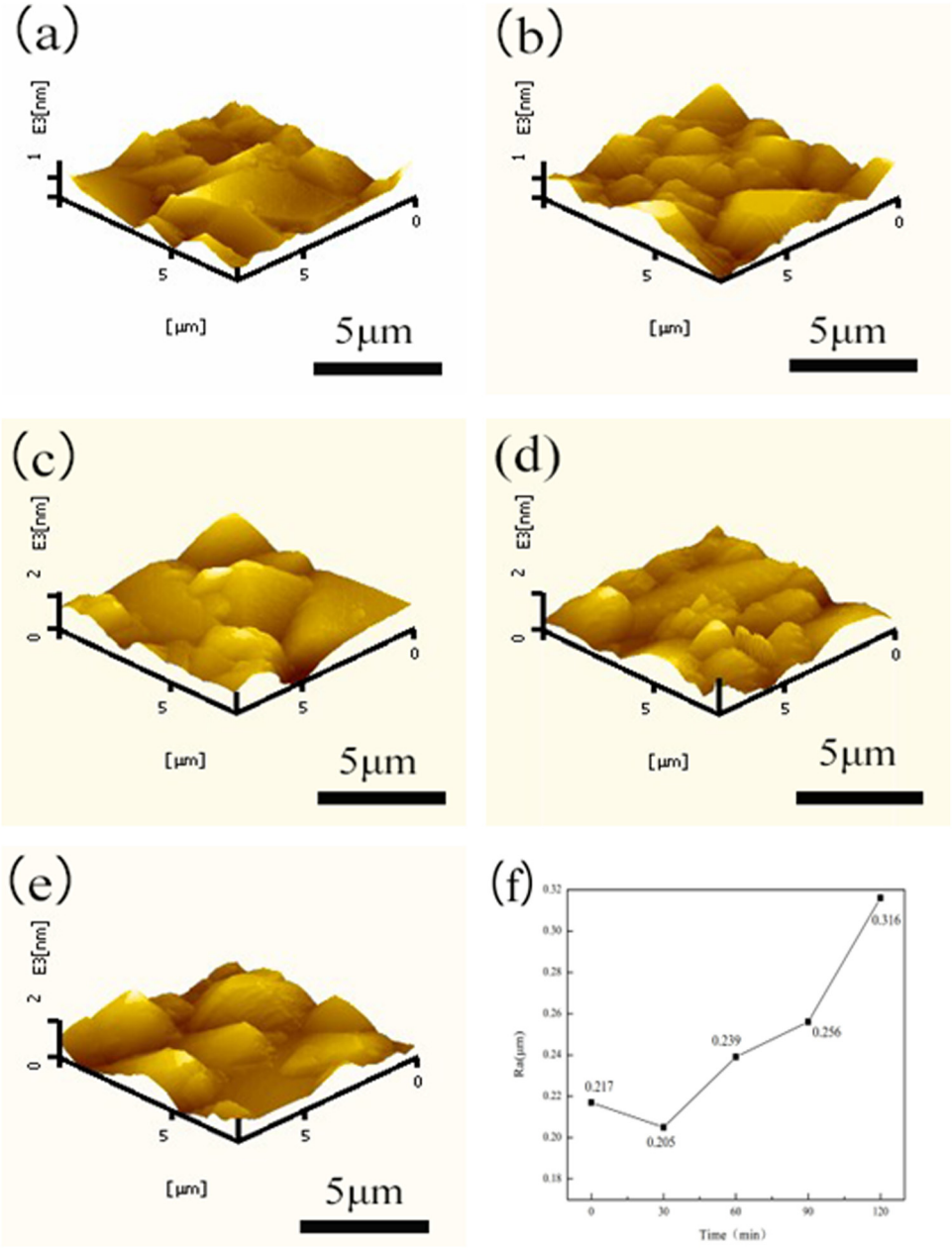

Figure 5: AFM images of samples etched at various times: (a) 0, (b) 15 min, (c) 20 min, (d) 60 min, (e) 90 min, and (f) 120 min.

finally continues to rise to 0.316 μm. Overall, first it showed a decreasing trend and then increased. This is consistent with SEM results.

3.3 Wettability and surface resistances

Angle contact measurement equipment was used to analyze the wettability of diamond samples before and after etching, which is illustrated in Figure 6. The contact angle of an unetched diamond sample with water is approximately 62.8°, as shown in Figure 6a, which reflected a marked hydrophilic character. Under these process conditions, a large amount of C–O exists on the surface of the prepared micron-scale diamond film. The oxygen terminal of diamond film shows hydrophilicity. Thus, surface bonds are the main cause of hydrophilicity. When the etch time increases to 30 min, the contact angle increases to 71.2° (Figure 6b). A part of the C–O bond on the surface of diamond film changes to C–H bond, which increases the contact angle of diamond film. Diamond film surface still behaves hydrophilically. As etching time increases to

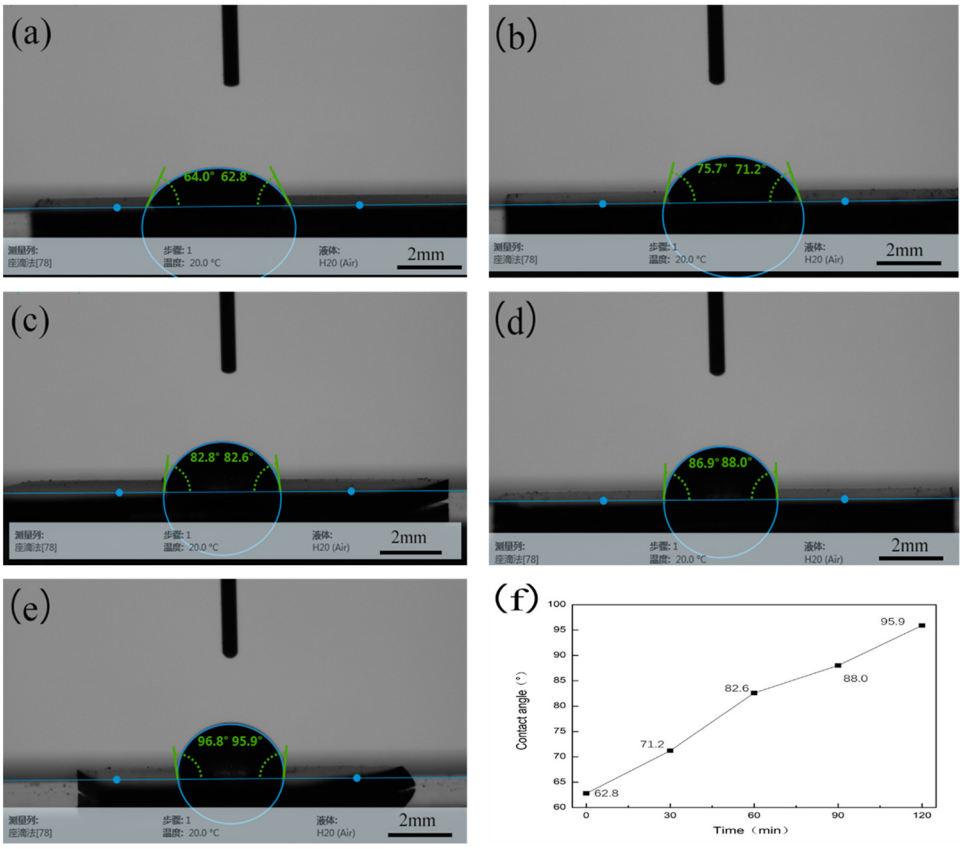

Figure 6: Diamond film contact angle test results: (a) 0, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, and (f) contact angle variation curve with time.

60 min, the contact angle was increased again to 82.6° (Figure 6c). The contact angle has been obviously increased compared with that before etching. As shown in Figure 6d, as the etching time increases to 90 min, the contact angle increases to 88°. Although the contact angle rises, it remains less than 90°, indicating that the diamond film surface is still hydrophilic. After etching for 120 min, the contact angle finally reaches 95.9° (Figure 6e). At this point, the surface of diamond film is hydrophobic. The hydrophilicity and hydrophobicity of the diamond film are mainly affected by the hydrogen and oxygen terminal functional groups. When the surface of diamond is oxygen terminal, the wettability appears as hydrophilic. The strong interaction between the water molecules and the terminal oxygen leads to the formation of new chemical bonds on the surface of an atom. When the surface of diamond is hydrogen terminal, it usually shows hydrophobicity. The degree of hydrophobicity is closely related to the type and number of chemical bonds on the surface.

The different bond states of carbon atoms make their surface terminal states different. After etching by hydrogen plasma, the surface of diamond film is damaged. The formation of C–H bond gradually replaces C–O bond, and C–O bond shows strong dipolar-polarization effects [29]. Finally, the conversion of oxygen terminal to hydrogen terminal is realized. A solid surface's wettability is primarily governed by two factors: chemical composition and roughness [30]. Hence, we increase the contact angle with increasing etching time. The surface of the diamond film was turned from hydrophilic to hydrophobic.

As shown in Figure 7, the resistivity of diamond was measured by a four-probe tester. The surface resistance of the micron-scale diamond film without hydrogen plasma etching is 3.71 MΩ. As is known to all, the diamond itself is an insulating material because of the high resistance nature. High resistance greatly limited being applications in the field of semiconductive electronic device. Nevertheless, after etching, the evolution of resistance is significantly changed. As the etch time increases to 30 min, the resistance value becomes 0.35 MΩ. This is consistent with the study by Liu [31]. The decreased surface roughness in diamond films leads to enhancement of carrier–carrier scattering effect. Thus, the carrier mobility is considerably increased and the resistance decreased obviously for

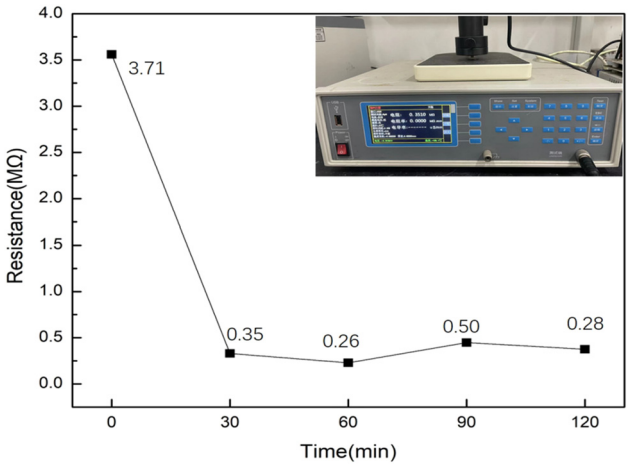

Figure 7: Micron-scale diamond film square resistance value with hydrogen plasma etching time.

diamond films. This is in a good agreement with our AFM results. This means that the hydrogen terminal is gradually forming on the diamond surface. This is consistent with the contact angle results. The square resistance did not change significantly for etching times between 30 and 120 min. Its value fluctuates at 0.26–0.50 MΩ.

The insulating diamond acquires conductive properties on the basis of hydrogen plasma treatment. The hydrogen terminal structure is formed on the surface. Combined with the analysis of wettability and surface resistance, the hydrogen-terminated diamond film after hydrogen plasma etching, the surface of which is hydrophobic, and the hydrogen-terminated surface producing dipoles, the energy required for electrons to be pulled out is reduced, and diamond film surface with negative electron affinity can interact with external receptors. The surface of diamond material loses electrons and forms P-type semiconductor hole orbits [32]. The surface resistance is reduced, and the conductivity is enhanced. Therefore, less than 30 min of etching time leads to an increase in carrier mobility. At this moment, the hydrogen terminal diamond can be realized semiconducting without ion implantation or doping.

4 Conclusion

In this article, the effects of hydrogen plasma treatment on the surface morphology and properties of micron diamond were characterized by SEM, AFM, contact angle tester, and four-probe resistance tester. The following conclusions are obtained.

In the prophase of etching, the electric field increases as the number of electrons at the crystal edge grows. The motion of electrons toward the surface of diamond films in the plasma is suppressed, and ions are attracted to bombard the edges of the crystal. Therefore, the crystal edge and the top of the grain are preferentially etched, and the surface roughness reduced. But when the etching duration exceeds 30 min, etching is mainly concentrated on the grain boundary. The outline of the grains became blurry, and the crystalline surface has a significant number of pits and steps. At the same time, the roughness slowly increases.

The contact angle also increases from 62.8° to 95.9° with the increase in etching time. The surface of the diamond film was turned from hydrophilic to hydrophobic. This is because the surface of the diamond film is destroyed following etching, and the formation of C–H bond gradually replaces C–O bond. Finally, the conversion of oxygen terminal to hydrogen terminal is realized.

The reduction in surface roughness of the diamond film 30 min before etching leads to the enhancement of carrier scattering effect. As a result, the carrier mobility of the diamond film is greatly increased, increases the H on the diamond film surface, slightly decreases the wettability, increases the surface roughness, and decreases the surface resistance to 0.35 MΩ. However, the resistance of the diamond film does not change significantly by extending the etching time and remains at 0.26–0.50 MΩ. Therefore, the factors affecting the surface resistance are multiple and need to be considered in a comprehensive manner.

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