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Morphological study of the localized growth of materials in dielectric barrier discharge*

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The localized growth of materials has been realized in a dielectric barrier discharge reactor in the mixture of acetylene and argon in previous work. In this paper, the morphology of the materials synthesized in the process is studied. The results indicate that the polymer's structure consists of three layers. The layer near the substrate is homogeneous with thickness of several micrometres; the middle layer is composed of dense bulges with height of about more than 10μm in average. The distance between two neighbouring bulges is about 230μm; the top layer is made up of a few large columns with the height up to 2mm, and with the average distance of about 3.5mm. The growth of the three layers corresponds to three types of discharge. The discharge mechanism is analysed through studying the morphology of the polymer. It can be deduced from the morphology that the first and second discharge phases should belong to the Townsend breakdown, and the last discharge phase should be explained on the basis of the streamer mechanism.

Keywords: Morphology, localized growth of materials, dielectric barrier discharge
PACC: 6150C, 5200, 5150

1. Introduction

Dielectric barrier discharge (DBD) is a kind of non-equilibrium alternating current gas discharge. The characteristic of DBD is that at least one of the electrodes is covered by dielectric. The layer of dielectric can restrict the rising of the discharge current. Compared with arc discharge, dielectric discharge can be distributed on the whole electrode uniformly even under high pressure, so DBD has been widely used in many scientific research fields and applications such as ozone generation, UV and VUV radiation, surface treatment, fabrication of new materials, elimination of poisonous gases and plasma display panels, etc.[1–3]

Depending on working conditions (such as the product of gas pressure and gas gap, the working gas, the electrode type, the waveform of the applied voltage, etc.), DBD can operate in different modes.[4] One of the modes is homogeneous glow-like discharge in appearance. But under most circumstances, DBD is composed of many narrow discharge filaments. These filaments are randomly distributed on the electrode. Under some special circumstances, these discharge filaments can interact with each other and pattern formation phenomenon can be observed in DBD.

The synthesis of new materials is becoming a hot issue in low temperature plasma study.[5] DBD is an effective way to produce low temperature plasma with the electronic temperature of about 10eV. So DBD is suitable to be used to synthesize new materials. Localized growth of materials on DBD in the mixture of acetylene and argon has been reported previously.[6] In the previous work, it was found that the discharges consisted of three different phases and plasma polymerization took place in the three phases of discharge. The material growth rate along the discharge filaments was much higher than that at other locations. The preliminary analysis of the material growth process was also reported in that paper.

In this paper, localized growth of materials is realized under similar experimental conditions. We analyse the morphology of the material synthesized in the discharges. The morphology of the material may play

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the role of a fossil that archaeologists use to determine the living creature in the past. In our experiment, the morphology of the material contains the information of discharge phases that can be used to deduce the spatio-temporal evolution of the discharges. On the other hand, knowing the relationship between the discharge phases and synthesized materials, it is easier to find new materials: that is to say, one can control the discharge phases to synthesize the wanted morphology of materials. Through the study of the morphology, obviously, we can link the different layers of the material with the different discharge phases. Moreover, the mechanism of each phase can be deduced by comparing the waveforms of the discharge pulses. The results show that wall charge on the dielectric is a key factor to influence the discharges of different phases.

2. Experiment setup

Figure 1 shows the experimental setup. The upper stainless steel electrode, 100mm in diameter, is connected to the reactor chamber and grounded through R_1. The lower electrode, also made of stainless steel and 50mm in diameter, is connected to a 3kHz ac power source. The upper electrode is covered with a glass plate with thickness of 3mm. The remaining gas gap between the two electrodes is 2mm. Resistors in the circuit are used for monitoring the discharge current and the voltage applied on DBD. They almost have no effect on the discharge circuit. The resistance of the resistors are: R_1=10Ω, R=95Ω, R_2=50MΩ, R_3=50kΩ. The chamber is evacuated with a mechanical pump to its limit, then the mixed gases of argon and acetylene are introduced at a flow rate of approximately 1000 and 500sccm, respectively. By adjusting the pumping speed, the pressure in the chamber is controlled at 35–50kPa.

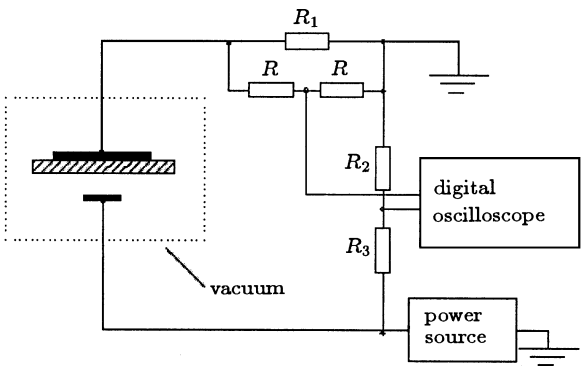


Fig.1. Scheme of experimental setup.

3. Experimental results

In the mixture of argon and acetylene, DBD undergoes three phases. At the beginning, it is homogeneous glow-like discharge, then the discharge changes to filamentary mode in which filaments are randomly distributed on the electrode area, and lastly (several minutes later), what is left are a few narrow filaments that localize at fixed locations to form a pattern. The diameter of the filaments in the pattern is about 100μm on average.

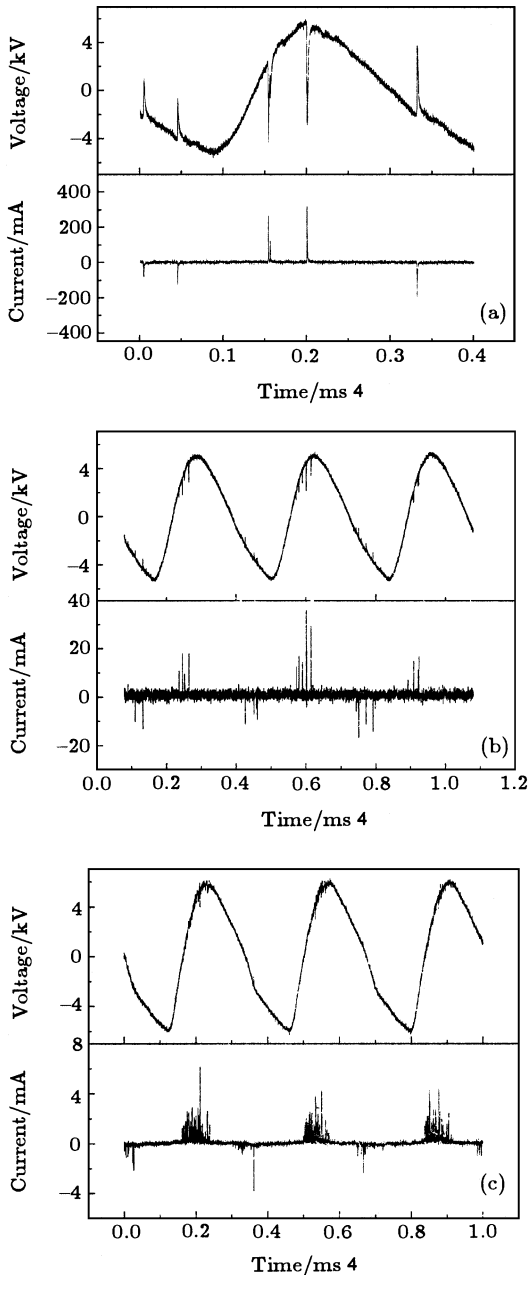


Fig.2. Relationship between the discharge current and the voltage during the three discharge phases respectively: (a) glow-like discharge phase, (b) filamentary discharge phase, (c) patterned phase.

Figure 2 shows the waveforms of the discharge current and the applied voltage in the three phases. From the figure, we can see that the discharge current pulses in each half cycle of the voltage are very rare in the first discharge phase, as shown in Fig.2(a). The number of discharge pulses becomes greater in the second phase than in the glow-like discharge phase, as shown in Fig.2(b). The number of discharge pulses in the third discharge phase reaches its maximum, as shown in Fig.2(c). Another interesting phenomenon is that the number of discharge current pulses becomes more and more differentiated for the positive and negative half cycle of the voltage in the course of the discharge development.

Figure 2 also shows the different voltage waveforms in the three discharge phases. From it we can see that the applied voltage is almost sinusoidal in the glow-like discharge. At the second phase, the applied voltage deviates from a sine wave. The distortion of the voltage is most evident in the third discharge phase.

In order to compare the individual pulses in the three discharge phases, we enlarge some part of the discharge pulses and Fig.3 shows the enlarged pulses in the three discharge phases respectively. It is evident that the width of individual pulses in the first phase is about 0.3ms, which almost equals that in the filamentary discharge phase. However, in the last discharge phase, individual pulses contain several smaller pulses with the appearance of damped high frequency oscillations. The width of these smaller pulses is only about 10 ns. The different width of discharge pulses implies that the three phases of discharges should have different physical mechanisms.

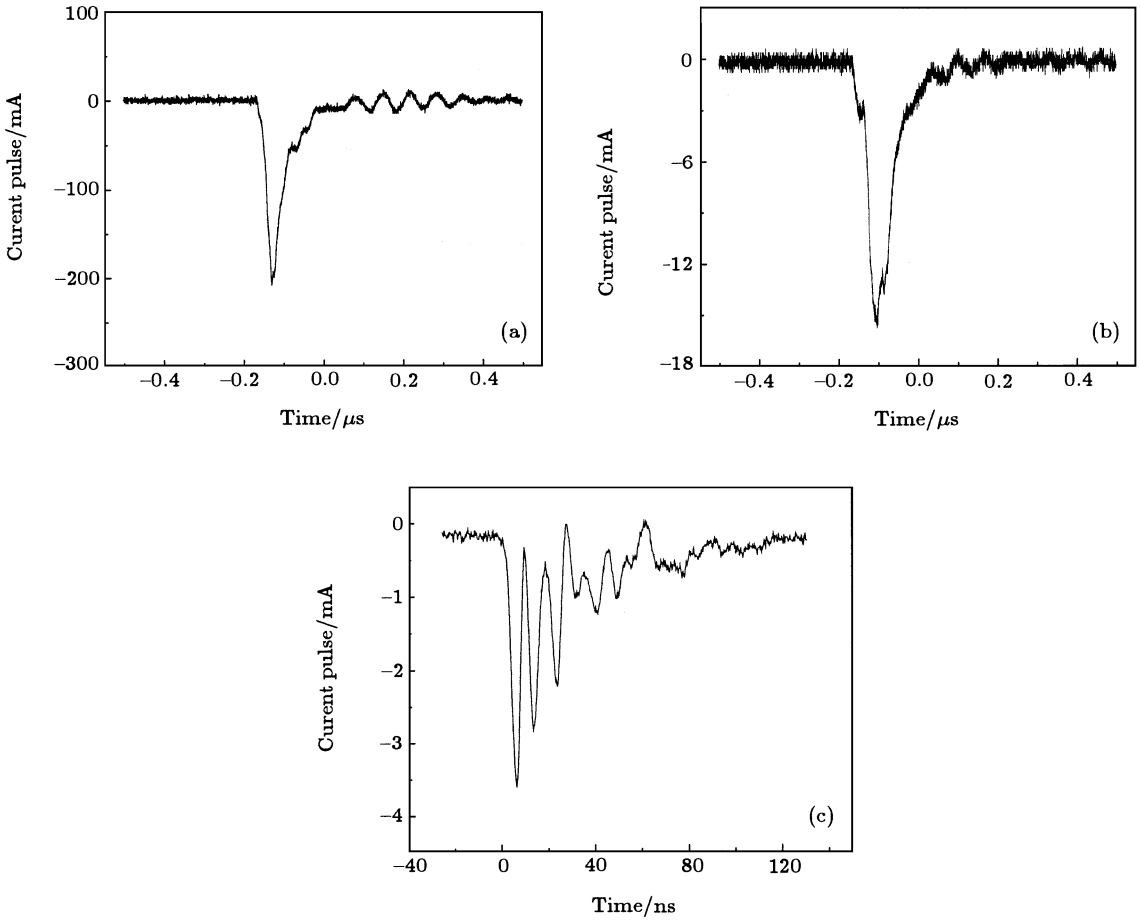


Fig.3. The shape of discharge current pulse in the three different phases: (a) an individual discharge pulse in the glow-like discharge phase, (b) an individual discharge pulse in the filamentary phase, (c) discharge current pulses in the patterned phase.

The synthesized material with the colour of dark coffee has three layers. We have made certain that the material is a kind of dielectric with very high impedance. The layer near the substrate is almost uniform, the thickness of which is several micrometres. The second layer consists of many bulges. Figure 4 is

a photograph of the second layer of the synthesized material, taken under microscope. We have analysed the morphology of the second layer and Fig.5 gives the structure of this layer. From Fig.5 it is easy to find that the height of the bulges is about 10μm and its diameter is some 50μm on average. The distance between two neighbouring bulges is about 190μm. Another layer is composed of a few big columns with the height of 2mm and its diameter is about 150μm. The distance of neighbouring big columns is about 3.5mm on average.

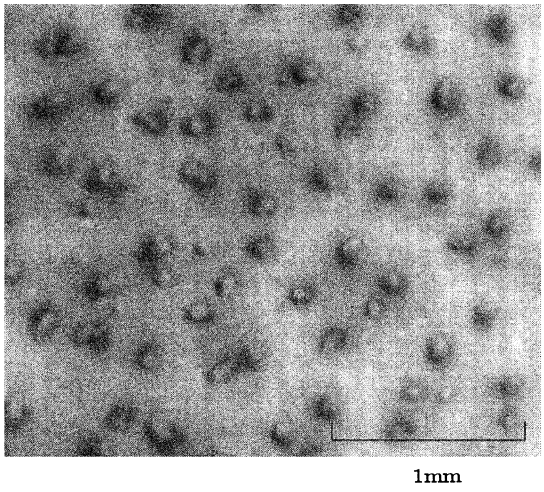


Fig.4. Photograph of the second layer under the microscope. The little dots correspond to bulges of the synthesized material.

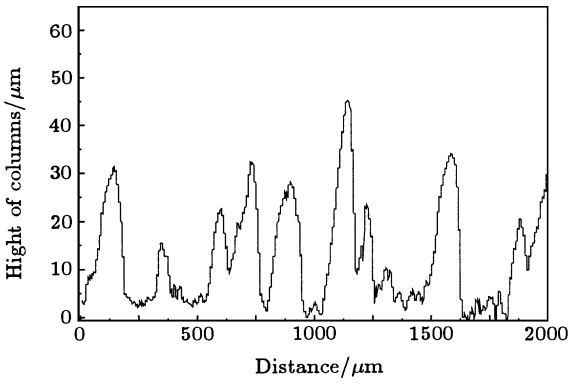


Fig.5. The morphology of the bulges.

It is also found that the synthesized materials on the glass plates have the appearance of floccules if both electrodes are covered by glass. Figure 6 gives its structure with the help of a microscope.

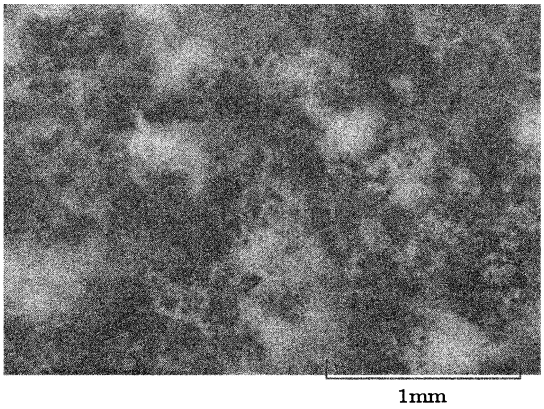


Fig.6. Photograph of flocculent materials synthesized on the glass plate when both electrodes are covered by glass.

4. Analysis and discussion

From the morphology of the material synthesized in the discharges and the three phases of the discharge, we deduce that the growth of different layers should correspond to different phases of discharges. The bottom layer should correspond to the homogeneous glow-like discharge. The growth of bulges should correspond to the phase of random filaments. The top layer of big columns would be synthesized at the discharge of pattern mode.

In order to clarify the growth mechanism of the material, we should grasp the effect of wall charges that accumulate on the dielectric. The accumulated wall charges can extinguish the breakdown because its electric field is opposite to the applied electric field; however, they will help the breakdown in the next half cycle of the applied voltage when the applied electric field changes its direction. This is the memory effect of wall charges in DBD.

We can imagine, if one location breaks down ahead of time, that wall charges will reduce the net field in the vicinity of the channel and discharges cannot happen in this area any more. However, when the next half cycle comes, the breakdown is prone to take place at the location of the channel. That is to say, DBD becomes filamentary because of the memory effect of the wall charges. From this point of view, it can be imagined that the stronger the memory effect is, the easier the DBD turns to be filamentary.

In our experiment, only one electrode is covered by dielectric, and wall charges can only accumulate on one dielectric at the first discharge phase, so the memory effect of wall charges in this discharge phase is not so strong that filaments can exist. Thus, the discharge looks homogeneous and the material syn-

thesized in this discharge phase should be uniform too. With the development of the discharge, the material synthesized on the electrode becomes thicker and thicker. Because it is a kind of dielectric, when the thickness of the material reaches a certain value, it seems that the other electrode is also covered by a dielectric and wall charges will accumulate on the surface of this dielectric. Comparing with the previous phase, wall charges will accumulate on the two plates of dielectric in the second discharge phase. It is natural to think that the memory effect becomes stronger in the second discharge phase compared with the first phase. Hence the discharge becomes filamentary in the second discharge phase.

We can also see that the memory effect in the second discharge phase is stronger than that in the first phase through comparison of the voltage waveforms in Fig.2. It is self-evident that the waveform of the voltage on the electrodes is determined by the applied voltage and influenced by the wall charges. Since the applied voltage is sinusoidal, the distortion from sine wave is posed by the wall charges. So we can imagine that the voltage deviates from the sine wave in the second discharge phase because more wall charges are accumulated on the dielectric in this phase compared with the glow-like discharge phase. This conforms to our explanation for the transition from the glow-like discharge phase to the filamentary discharge phase.

In the second discharge phase, filamentary channels have higher plasma density than other locations and the head of the electric avalanche impacts on the local substrate, where it causes higher temperature and activation of the surface, which makes the material growth rate higher than at other locations on the substrate. So the bulges grow on the uniform layer. Then the morphology is changed and the wall charges will accumulate on these protrusions.

The first two phases of discharge belong to the Townsend breakdown mechanism. In these phases, the electric field is nearly uniform and the multiplication of electrons (or the creation of new electrons) depends on the collisions of high-speed electrons with stationary atoms. The development of discharge current depends on the drifting speed of electrons. So in Figs.3(a) and (b) the width of individual discharge current pulse in the two discharge phases are almost equal. However, as the height of protrusions increases, the distortion of electric field increases too. When the distortion reaches a certain extent, the discharge will turn into the streamer mechanism.[7] In the streamer mechanism, the development speed of discharge current does not rely on the drifting speed of electron, but depends on the light speed because most secondary electrons are generated by the ultraviolet radiation of the discharge. So the development of discharge current in the third discharge phase is much faster than that in the first and second discharge phase. The consequence is that the width of discharge current in this phase is much shorter compared with the previous discharge phases. At present, we have poor understanding of why these smaller pulses oscillate with damping at high frequency.

In the streamer discharge, the plasma density is very high and the temperature of the location where the discharge hits is pretty high too. So the growth rate of material at these locations is much higher than that at other locations. The discharges of neighbouring filaments compete strongly, and the eventual consequence of competition is that only a few streamer filaments can exist. These persistent filaments have a regular distance between neighbouring filaments and a pattern formation phenomenon can be observed in this discharge phase in our experiment. At this stage, the preferential, fast growth of some of the bulges leads to the formation of a third layer, consisting of a small number of more or less uniformly distributed large columns. Therefore, the top layer of synthesized material only consists of a few large columns that have regular distribution.

Consequently, the different layers of synthesized materials would correspond to the three types of discharges. According to this supposition, we can determine the growth rate of each layer. The growth rate of the bottom layer is about 0.5μm per minute. The growth rate of small columns is approximately 2μm per minute. The growth rate of large columns is about 21μm per minute. That is to say, the growth rate of materials in the third discharge phase is much faster than that in the first and second discharge phases. We think the difference of growth rates can be attributed to the different discharge mechanisms of the three discharge phases.

5. Conclusion

In this paper, we studied the morphology of localized material synthesized in the mixture of argon and acetylene by DBD. The growth of three layers of material corresponds to different discharge. The mechanism of different phases of discharge is discussed in de-

tail and we believe wall charges are important for the transition from the homogeneous glow-like discharge to random filamentary discharge and then to the patterned discharge. The morphology of the materials is determined by the three discharge phases and the growth rates are given in the paper. We believe the conclusions are important for the growth of localized materials.

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