Preparation and characterization of PTFE coating in new polymer quartz piezoelectric crystal sensor for testing liquor products*

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A new method was developed based on the electron beam vacuum dispersion (EBVD) technology to prepare the PTFE polymer coating of the new polymer quartz piezoelectric crystal sensor for testing liquor products. The new method was applied in the new EBVD equipment which we designed. A real-time system monitoring the polymer coating's thickness was designed for the new EBVD equipment according to the quartz crystal microbalance (QCM) principle, playing an important role in preparing stable and uniform PTFE polymer coatings of the same thickness. 30 pieces of PTFE polymer coatings on the surface of the quartz crystal basis were prepared with the PTFE polymer ultrafine powder (purity $\geq$ 99.99%) as the starting material. We obtained 30 pieces of new PTFE polymer sensors. By using scanning electron microscopy (SEM), the structure of the PTFE polymer coating's column clusters was studied. One sample from the 30 pieces of new PTFE polymer sensors was analysed by SEM in four scales, i.e., 400×, 1000×, 10000×, and 25000×. It was shown that under the condition of high bias voltage and low bias current, uniformly PTFE polymer coating could be achieved, which indicates that the new EBVD equipment is suitable for mass production of stable and uniform polymer coating.

Keywords: PTFE coating, electron beam vacuum dispersion, mass production of polymer coating

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1. Introduction

Liquor products are special beverages that are enjoyed by many people; especially, Chinese spirits are very famous throughout the world, of which there are many types, such as Luzhou liquor, Fen liquor, Maotai liquor, and so forth. Micro-constituents such as esters, acids, phenols, and carbonyl compounds in Chinese spirits comprise just 2% of the total composition, but they are the key factors that affect the flavor. We can distinguish the Chinese spirits' myriad components via testing the micro-constituents.[1] We designed a testing instrument to test Chinese spirits. The instrument's main working component is made up of eight new polymer quartz piezoelectric crystal sensors.[2] The new sensor based on the principle of quartz crystal microbalance (QCM) takes a quartz piezoelectric crystal as the basis and a polymer material as the surface coating.

Polymer coating has high sensitivity for testing micro-constituents in Chinese spirits.[3] Due to the polymer materials' diversity and stability, they have become important starting materials for coating preparation. The polymer material can adhere to the surface of the quartz crystal basis. Many methods have been proposed to prepare polymer coating, including spin- or spray-coating,[4–7] transfer printing,[8–11] dipcoating,[12] electrophoretic deposition,[13] Langmuir–Blodgett (L–B) assembly,[14,15] rotating coating, and self assembling.[16] As we know, the sensitivity of the new polymer quartz piezoelectric crystal sensor for testing Chinese spirits is greatly affected by the thickness of the polymer coating adhered to the quartz crystal basis' surface. However, the above-mentioned methods have difficulty in preparing polymer coatings with the same thickness. Therefore, they are unsuitable for the required mass production of stable and uniform polymer coating.

We developed an efficient method based on the electron beam vacuum dispersion (EBVD) technology to prepare polymer coatings with the same thickness on quartz crystal. Especially, a real-time polymer coating thickness monitoring system was designed. We can obtain a polymer coating of arbitrary thickness on the surface of the quartz crystal, and monitor the growth status of the polymer coating in real-time. In this work, we prepared the polytetrafluoroethylene (PTFE) polymer coating, which is 35 μm thick on the surface of the quartz crystal. It is a new PTFE polymer quartz crystal sensor to effectively test Chinese spirits.[2] By using scanning electron microscopy (SEM) photos, we discussed the structural parameters of the PTFE polymer coating's column clusters.

2. The new EBVD equipment

As shown in Fig. 1, for the preparation of the polymer coating, we designed a new EBVD equipment based on the improved EBVD technology. The new EBVD equipment con-

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tains an electron beam deposition system in the vacuum chamber (EBVDS), a control system (CS), and a real-time monitoring system of polymer coating's thickness (RTMS). Especially, the real-time monitoring system of polymer coating's thickness we designed plays an important role in preparing a stable and uniform polymer quartz piezoelectric crystal sensor for testing Chinese spirits.

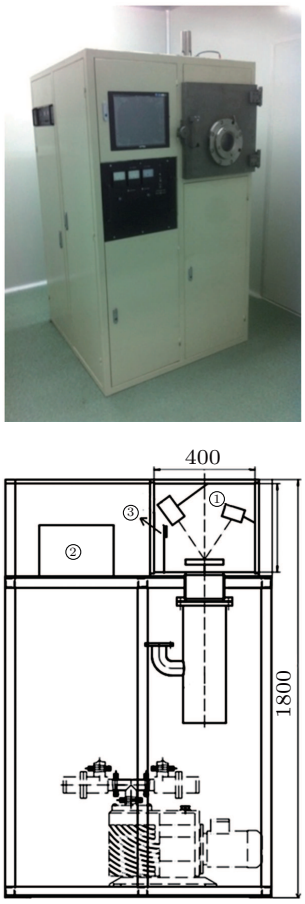


Fig. 1. (color online) The new EBVD equipment for preparation of polymer coating.

The QCM based sensor measures the mass per unit area by measuring the change in the frequency of a quartz crystal resonator. The resonance is disturbed by adding or removing mass deposited at the surface of the resonator. According to the principal of the QCM, the change in the oscillation frequency of the piezoelectric crystal is related to the mass deposited on the surface, which is described by the Sauerbrey equation

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}}\Delta m = N\Delta m, \tag{1}$$

where $N = -2f_0^2/(A\sqrt{\rho_q\mu_q})$, f_0 is the resonant frequency (Hz), Δf is the frequency change (Hz), Δm is the mass change (g), A is the piezoelectrically active crystal surface area (cm^2), ρ_q is the density of quartz ($\rho_q = 2.643$ g/cm^3), and μ_q is the shear modulus of quartz for AT-cut crystal ($\mu_q = 2.947 \times 10^{11}$ g·cm^{-1}·s^{-2}).

From the Sauerbrey equation (1), we can obtain

$$\Delta f = N\Delta m = N\rho_p S_q \Delta d = K\Delta d, \tag{2}$$

where $K = N\rho_p S_q$, ρ_p is the density of the polymer ($\rho_p = 2.22$ g/cm^3 for PTFE polymer ultrafine powder), S_q is the area of the deposited polymer on the quartz crystal (cm^2), and Δd is the polymer coating's thickness (10^{-4}cm). Equation (2) indicates a linear relationship between the frequency change and the change of the polymer coating's thickness.

According to Eq. (2), we designed a real-time monitoring system for the polymer coating's thickness in the new EBVD equipment. The system is composed of three parts, a quartz crystal vibration frequency measurement device, a transmission line of signals, and an analysis software of the polymer coating's thickness. We know that the particles of the polymer material distribute uniformly in the full vacuum chamber due to the motivation by the electron beam. So we consider that the polymer coating on the surface of the quartz crystal plate in the electron beam deposition system has the same thickness. Figure 2 shows the quartz crystal vibration frequency measurement device, which is the key component in the real-time monitoring system of polymer coating's thickness. We can capture the frequency change of the standard quartz crystal sample during the polymer coating growth in real-time, and output the thickness of the polymer coating by using the analysis software. Therefore, we can monitor the thickness of the polymer coating on the surface of the quartz crystal plate in the electron beam deposition system in real-time.

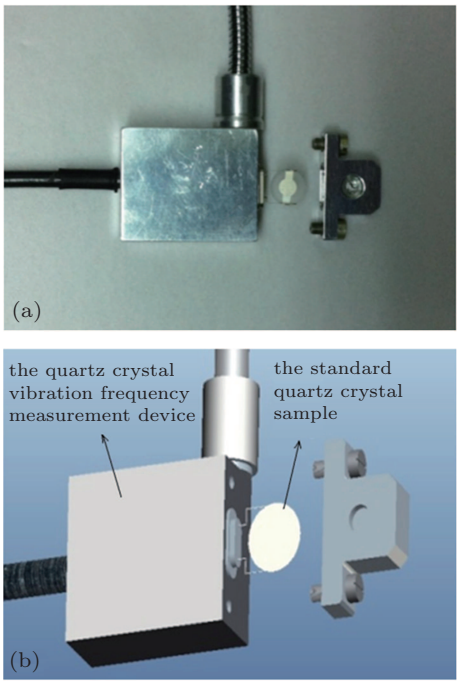


Fig. 2. (color online) (a) Photo and (b) model of the quartz crystal vibration frequency measurement device.

3. Preparation and characterization of the PTFE coating

3.1. Materials

PTFE polymer ultrafine powder (purity $\geq$ 99.99%) with primary particle size of 2–5 μm, bulk density of 0.5 kg/L, and specific gravity of 2.22 g/cm^3 was used. The AT-cut quartz crystal plate was applied as the basis with a diameter of 8 mm, a thickness of 130 μm, and a resonant frequency of $f_0 = 10$ MHz.

3.2. Preparation of PTFE polymer coating

We used the new EBVD equipment to prepare the PTFE polymer coating on the surface of the quartz crystal plate. Figure 3 shows the position diagram of the electron gun, the crucible, and the substrate table in the EBVDS. The distance between the electron gun and the crucible is 15 cm, and the distance between the crucible and the substrate table is 10 cm.

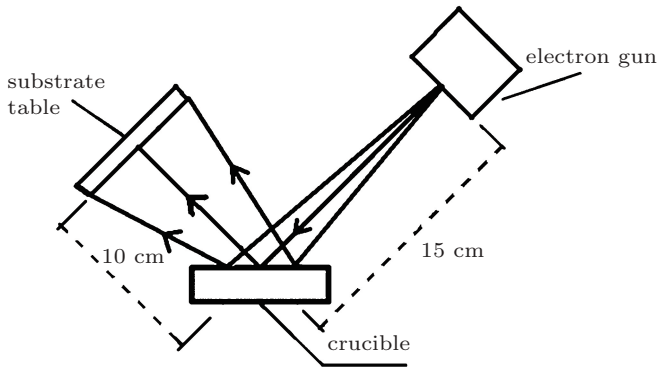


Fig. 3. The position diagram of the electron gun, the crucible, and the substrate table.

The diffusion pump of the new EBVD equipment was preheated for about 1 h. When the diffusion pump's temperature reached 80 °C, we put 5 g of PTFE polymer ultrafine powder into the crucible, and installed the 30 pieces of AT-cut quartz crystal plates on the substrate table in the vacuum chamber. We set the density of the PTFE polymer ultrafine powder at 2.22 g/cm^3 in the analysis software.

After the above preparatory work, the vacuum pump in the EBVDS was started. After about 5 min, the pressure in the vacuum chamber reached 3.2×10^{-3} Pa. Then the electron beam deposition system and the real-time polymer coating thickness monitoring system were started. We set the electron beam's bias current at 60 mA in the electron gun and slowly increased the bias voltage of the power supply to 1.3 kV. We found by using the real-time monitoring system that the thickness of the polymer coating on the surface of the quartz crystal plate varied linearly with time. It showed that the PTFE ultrafine powder adheres to the surface of the quartz crystal plate in the particle state due to the motivation by the electron beam.

About 20 min later, the real-time monitoring system showed that the thickness of the PTFE polymer coating on the surface of the quartz crystal reached 35 μm. This means that 30 pieces of new polymer quartz piezoelectric crystal sensor were obtained, and the thickness of the PTFE polymer coating on the surface of the quartz crystal plate was 35 μm. Figure 4 shows the new PTFE polymer quartz crystal sensor obtained.

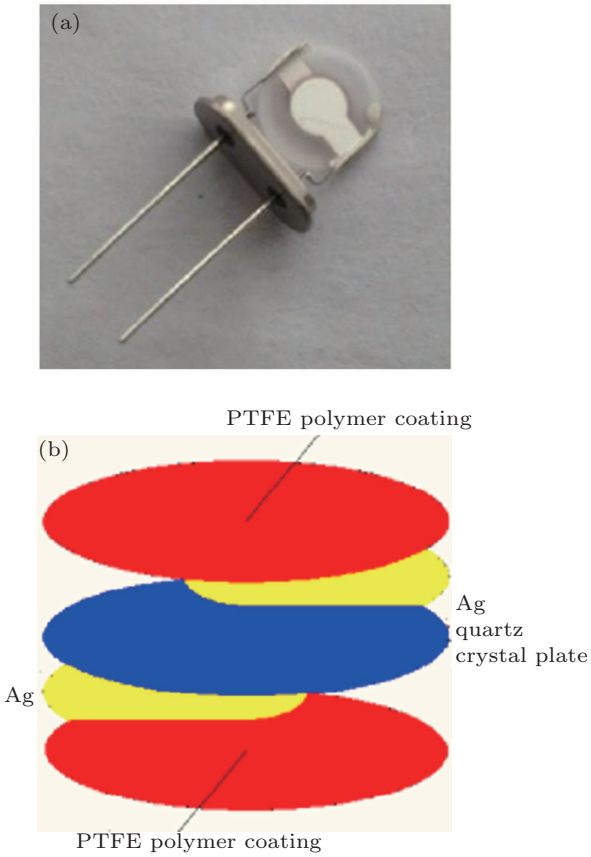


Fig. 4. (color online) (a) Photo and (b) model of the new PTFE polymer quartz piezoelectric crystal sensor.

3.3. Characterization of the new PTFE polymer quartz piezoelectric crystal sensor

The structure of the PTFE polymer coating was characterized using the SEM (S-4700) made by Hitachi limited. In order to avoid the destruction of the PTFE polymer coating due to the strike of the high speed electron released by the electron beam of the SEM, we selected the low accelerating voltage ranging from 1 kV to 5 kV for observing the structure of the PTFE coating. One sample from the 30 pieces of new PTFE polymer sensors was analyzed by SEM in four scales, i.e., 400×, 1000×, 10000×, and 25000×.

Figure 5 shows 400× and 1000× surface morphologies of the PTFE polymer coating. In the photos, a uniform surface of the PTFE polymer coating is exhibited. The observations reveal that uniformly sized and spaced PTFE polymer column clusters could be formed on the quartz crystal surface. All the

diameters of the PTFE polymer column clusters are around 5 μm.

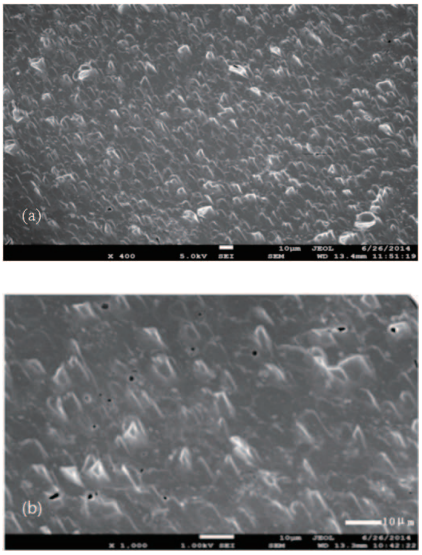


Fig. 5. (color online) Surface morphologies of the PTFE coating: (a) 400×, (b) 1000×.

Figure 6 shows 10000 × and 25000× surface morphologies of the PTFE coating. In the photos, we find many condensation nuclei that are tiny PTFE polymer particles. With the accumulation of the tiny deposited PTFE polymer particles, the tiny PTFE polymer particle grows via the three-dimensional Volmer-Weber mode on the surface of the quartz crystal.

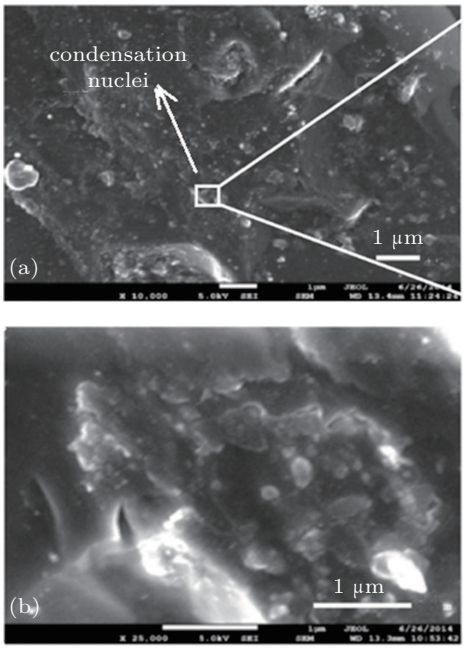


Fig. 6. (color online) The condensation nuclei of the PTFE coating: (a) 10000×, (b) 25000×.

4. Conclusion

1) By employing the new EBVD equipment we designed, PTFE polymer coatings were prepared on the quartz crystal plates at bias voltages of the power supply ranging from 1250 V to 1300 V and bias currents ranging from 55 mA to 60 mA. During this process, the PTFE polymer coating's thickness was measured in real-time. Then stable and uniform polymer coatings with the same thickness were obtained on the surface of the quartz crystal basis.

2) The PTFE polymer column clusters were studied with the SEM photos in four scales, i.e., 400×, 1000×, 10000×, and 25000×, showing that uniformly sized and spaced PTFE polymer column clusters could be formed and the PTFE polymer tiny particles grow via the three-dimensional Volmer–Weber mode on the surface of the quartz crystal, and all the diameters of the PTFE polymer column clusters are around 5 μm.

3) The above results indicate the new EBVD equipment is suitable for the mass production of stable and uniform polymer coatings, significantly expanding their large scale application. It provides a guidance for manufacturing new polymer quartz piezoelectric crystal sensors for testing liquor products such as Chinese spirits effectively, consistently, and objectively.

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