Binary Channel SAW Mustard Gas Sensor Based on PdPc$_{0.3}$PANI$_{0.7}$ hybrid Sensitive Film

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Abstract. This paper discussed the working principle of binary channel surface acoustic wave (SAW) lithium niobate piezoelectric chip detecting mustard, established the mathematic model of beat frequency output $\Delta f$ and the mustard gas density $\delta$. The MEMS craft solved the parameters of the binary channel SAW chip such as its interdigital electrode number was 15~25 couple, width and spacing were both 25$\mu$m, degree of overlapping was 2mm, fundamental frequency was 10~35MHz, frequency-domain width was 5~20Hz, and its back pt hot film’s. According to TG-DSC thermal analysis, vacuum coating craft was adopted to solve the hybrid sensitive film forming craft parameter of PdPc$_{0.3}$PANI$_{0.7}$ (phthalocyanine palladium$_{0.3}$ Poiyaniline$_{0.7}$). The micro-appearance of sensitive film was analyzed through SEM. The sensor’s sensitivity and response characteristic were tested and analyzed: appear linear change, its response time is less than 5min while its recovery time is less than 8min.

1. Introduction

Mustard gas is a typical vesicant agent in chemical agent. It has extensive damage to the animal and humanity such as alkylation, gene and cell poisoned, nervous system destructed and so on, is extremely dangerous. The war leaves behind with terrorism create injury to people, and even death events are also obvious to all. So study on the sensor which detects mustard gas has reality and security significance [1]. It has been more than fifty years’ research about the detecting method of chemical poison. The main are chemical analysis and laser detection, there are shortcomings such as big volume, heavy weight, non-portable, long detect period, high fatalness and bad flexibility etc. So, developed country has already commenced to explore third-generation chemical poison detecting method, which requires portable, quick response, high sensitivity, high stability, low price, also more automated and miniaturized. Micro sensor has just satisfied these requirements. It is realized through the combination of chemical sensor and advanced nanometer technology, MEMS, organic LB thin film technique.

For Surface Acoustic Wave (SAW) component has high sensitivity to outside environment, especially to air components, temperature and pressure, it can be manufactured to be various high performance sensor which has extensive use, such as SAW temperature sensor, SAW pressure sensor and SAW chemical sensor [2]. SAW gas sensor has had more than ten years’ history until now, but no matter its basic structure, detecting mode or its gas-sensitive chemical film’s selection and exploitation, are all waiting for further growth and perfecting. This paper discussed the working
principle of binary channel surface acoustic wave (SAW) lithium niobate piezoelectric chip detecting mustard, established the mathematic model of beat frequency output $\Delta f$ and the mustard gas density $\delta$. The MEMS craft solved the craft parameter of the binary channel SAW chip. Vacuum coating craft was adopted to solve the hybrid sensitive film forming craft parameter of PdPc$_{0.3}$PANI$_{0.7}$ (phthalocyanine palladium$_{0.3}$ Poianiline$_{0.7}$). The micro-appearance of sensitive film was analyzed through SEM. The sensor’s sensitivity and response characteristic were tested and analyzed.

2. Working principle and mathematic model

The basic components of SAW sensor are piezoelectric substrate and a couple of metal interdigital electrodes deposits on it. There is an interdigital transducer on both sides of the substrate each. One is surface acoustic wave emitter, which transfers the electric signal acted on the transducer into surface acoustic wave signal with the same frequency. Another one is receptor, which receives the acoustic signal that produced by emitter delivered by substrate surface, and transfers it into electric signal [3]. Figure 1 is the structure and detecting principle of binary channel SAW. It photoetched two couples of SAW delay line on a single-sided polished quartz plate, they are separately connected to low-noise amplifier to compose VHF SAW oscillator. After frequency mixing and filtering, differential frequency signal which outputted corresponding to the poison concentration is obtained. Binary channel SAW is for the self-compensation to the circumstance (temperature, humidity etc).

\[ f = n / (\tau_o + \tau_e), \]

where $\tau_o$ is SAW propagation delay time, ms; $\tau_e$ is amplifier delay time, ms; $n$ is positive integer. Generally, $\tau_o >> \tau_e$, so the formula above approximate to

\[ f \approx n / \tau_o, \]
According to surface wave theory, the relation between propagating frequency and receiving frequency of surface wave on quartz plate is:

\[ f_i = \alpha f_c \]  

(3)

where \( f_c \) is propagating frequency, it is constant in fixed circuit, MHz; \( f_i \) is receiving frequency, MHz; \( \alpha \) is the parameter related to the mid-medium of transducer.

Because \( \alpha \) is the parameter related to the mid-medium of the two transducer, as to sensor chip’s reference object, air is the mid-medium. When the sensor is working, \( \alpha \) is constant, so receiving frequency \( f_i \) is constant; As to sensor chip’s sensitive object, the sensitive adsorption layer related to poison is the mid-medium. When the sensor is working, once the adsorption layer contacts poison, \( \alpha \) changes, and so do the receiving frequency \( f_i \).

Therefore, when the oscillating frequency of the two oscillators are inputted into mixer, differential frequency output \( \Delta f \) is obtained:

\[
\Delta f = |f_{j2} - f_{j1}| \\
= f_c / \delta - \alpha (\varepsilon \geq \alpha) \\
\approx n\delta / \tau_o - n\alpha / \tau_o ,
\]

(4)

for \( n\alpha / \tau_o \) is constant, suppose \( \beta = n\alpha / \tau_o \), then

\[ \Delta f = n\delta / \tau_o - \beta , \]

(5)

Where \( \Delta f \) is differential frequency output, MHz; \( f_{j2} \) is the channel SAW receiving frequency of smear sensitive object, MHz; \( f_{j1} \) is the channel SAW receiving frequency of reference object, MHz; \( \delta \) is the parameter related to mid-sensitive object of transducer; \( \alpha \) is the parameter related to the mid-medium of transducer.

So, it appears linear relation between differential frequency output \( \Delta f \) and \( \delta \). Through detecting the differential frequency output \( \Delta f \), the kind and concentration of the poison will be calculated.

3. The fabrication and analyzing of sensor

3.1. Chip fabrication using MEMS technology

In order to reduce the dissipation in signal conversion and transmission, increase component’s working efficiency and stability, ideal piezoelectric materials should have biggish surface acoustic wave-electromechanical coupling coefficient, lesser surface acoustic wave transmission attrition rate, well temperature stability, and their crystal grains should be small, have high uniformity and repeatability. Lithium niobate crystal, which has well temperature stability, higher material uniformity and repeatability, biggish electromechanical coupling coefficient, is adopted as piezoelectricity material. It is relatively ideal substrate material.

MEMS craft is adopted to fabricate sensor chip. Before deposit metal interdigital electrodes, substrate surface should be optical polished. Then through vacuum coating method to coat a layer of metal film on the polished piezoelectricity substrate (the thickness is about 0.1–0.3μm), after more than ten procedure such as polish, cleaning, coating, photoetching, etching etc, the interdigital electrodes with required pattern and dimension are fabricated. The interdigital electrodes parameters of the piezoelectricity substrate SAW component are: its interdigital number is 15–25 couple, its width and spacing are both 25μm, its degree of overlapping is 2mm, its fundamental frequency is 10–35MHz, its frequency-domain width is 5–20Hz. At the same time, for the sensitive film needs to work in 40–60°C, a thickness of 500nm pt film is coated on the substrate’s back through magnetron sputtering. Then after photoetching, backwash, the required pattern is fabricated. In order to reduce interference wave, organic silicon rubber filter material is smeared on both sides of the interdigital electrodes. The experiment indicates that the filter material has extremely improved the surface acoustic wave signal.
3.2. The immobilization and characterization of the sensitive film

The sensitive film is the key of the SAW gas sensor. The interaction between measured gas and sensitive film maybe feeble physical adsorption or strong chemical adsorption, even is stronger chemical reaction. The ideal interaction should be quick, specific and reversible. In catalysis, take phthalocyanine palladium (PdPc), polyaniline (PANI) and a little dopant with mixing ratio of 3 : 7 (mg) as materials, through liquid phase macromolecule synthesize technology to hybridize in molecular level, and then purified and dried, a new type of organic semiconductor sensitive material PdPc_{0.3}PANI_{0.7} is synthesized.

In order to keep the intrinsic property, different thermal analysis to the sensitive material is carried out. Figure 2 is the TG-DSC thermal analysis of the PdPc_{0.3}PANI_{0.7} sensitive material. The analysis indicates that its weightless temperature is at 300°C~400°C, once temperature rises, heat releases, exothermic peak is also in the range of weightless temperature. This means there is plenty of gas adsorbed on the sensitive material surface, gas is desorbed release heat accompany with the rising temperature, and sensitive material begin decomposing at 300°C, over at 400°C, releasing plenty heat, over at 400°C and drive to stable. So, the solidification temperature should be controlled below 300°C.

![Figure 2. the TG-DSC thermal analysis of the PdPc_{0.3}PANI_{0.7} sensitive material.](image)

Put the sensor chip onto the upper mask plate of evaporating dish in vacuum coating machine. In 2×10^{-5}Pa, with 20A heating current, evaporating for 5~2min, PdPc_{0.3}PANI_{0.7} (phthalocyanine palladium_{0.3} Polyaniline_{0.7}) hybrid sensitive film of 500~800nm-thick is formed. Figure 3 is the SEM surface appearance of the sensitive film in 5000 times. It appears 1μm width-striation, continuous, multihole, homogeneously distributed dopant and latticework surface state, this gives well activity and gas desorption ability to the film.

![Figure 3. the SEM surface appearance of the PdPc_{0.3}PANI_{0.7} sensitive film.](image)

4. Test result and analysis

Put the sensor into testing box, with 0.5V heating voltage, its sensitivity and response - recovery characteristic are to be tested in dynamic method. Figure 4 is the sensitive characteristic of SAW sensor, its variation regularity appears N type linear change. Its sensitivity is about 105 kHz...
/(mg/m³) after calculation. Figure 5 is the response-recovery curve of the sensor, its response time is less than 5min while its recovery time is less than 8min.

Presently, the sensitive mechanism of PdPc0.3PANI0.7 hybridized sensitive film is not very clear, generally drive to semiconductor theory. Organic semiconductor’s π electron has low transition energy, the whole molecule has low capacitance energy and high polarized energy, so it is easily to make charge transfer with electron-defect gas so as to generate cavity on material surface, result in conductance increasing. When reducing gas is adsorbed, the conductance decreases. The experiment data indicate the principle and craft are feasible, but its stability, mechanism and the recognition to other poison still need further study.

5. Conclusion
Take binary channel surface acoustic wave (SAW) lithium niobate piezoelectric chip detecting mustard as working principle, established the mathematic model of beat frequency output Δf and the mustard gas density δ. The MEMS craft has solved the craft parameter of the binary channel SAW chip. Vacuum coating craft was adopted to form well PdPc0.3PANI0.7 hybrid sensitive film on electrode and the micro-appearance of sensitive film was analyzed. The sensor’s sensitivity and response characteristic were tested and analyzed, and it appeared N type linear variation regularity. This study results supply new method to potable detecting of chemical poison such as mustard gas etc, and also make foundation for theory and applied study of SAW and organic semiconductor sensor.
Acknowledgments
This work was supported by Heilongjiang Province scientific and technological project (Grant No.: GC03A121), National Natural Science Foundation of China (Grant No.: 60272002) and National 973 project (Grant No.: 2003ccc01100).

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