Real-time sensing of trace TNT with acoustic surface wave method based on the modified interdigital transducer electrodes*

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2,4,6-trinitrotoluene (TNT) has a strong explosive force and environmental toxicity, with the increasing threat of terrorist attacks worldwide, the high sensitivity detection of nitroaromatic explosives has become an urgent problem to be solved, and now the commonly used detection method is to use the optical principle, combined with large and expensive equipment to detect it. In order to detect the content of TNT in bad environment quickly and in real time, surface acoustic wave technology was proposed to detect different concentrations of TNT. In this paper, an ultra-sensitive TNT sensor was fabricated based on the surface acoustic wave technique. Specific detection of TNT was achieved by recognizing the shift of resonance frequency. Moreover, the whole process for the detection was done in 30 min, dedicating the rapid/real-time application of the sensor. This study focused on the transfer characteristics of resonance frequencies at different concentrations. The frequency of surface sound waves varies greatly at high concentration because the modified IDT (interdigital transducers) electrodes were utilized, which is easy to work under different concentrations of TNT. The proposed sensor has the advantages of real-time, simple and convenient detection, which provides a valuable method for the real-time detection of TNT.
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2, 4, 6-trinitrotoluene (TNT), or trinitrotoluene for short, is a light yellow crystal, insoluble in water and low cost. It is one of the most widely used explosives in the world and is often used in explosive terrorist events. Current common detection technologies include ion mobility spectrometer (IMS)[1], mass spectrometry (MS), X-ray scattering tomography[2], nuclear power quadrupole resonance method, neutron detection technology, surface-enhanced Raman scattering spectrometer (SERS)[3], and so on. Ion mobility spectrometer is used to ionize the working gas in the ion mobility detector under the action of ion source. The ionized carrier gas interacts with the sample gas to ionize the sample gas and identify the types of ions through the different migration velocity. Mass spectrometry detection of explosives has been a relatively mature technology. The principle is that ions with different mass charge ratios (the ratio of mass to charge) have different forces in the magnetic field, and their movement directions are also different, leading to their separation. The types and relative contents of ions can be determined through separate capture and collection. X-ray imaging technology projects X-ray energy and collects image data. The imaging results reflect the absorption degree of X-ray by the target object and show the projected figure, but X-ray is harmful to human body. The quadrupole moment resonance method of nuclear power uses the device to generate microwave pulses acting on explosive materials to excite atoms. These atoms resonate under the action of the coil magnetic field to generate energy waves. After the energy waves are processed by computer, whether there are explosives can be detected and the type of explosives can be determined. Neutron detection technology uses the interaction between seed pulse beam and nuclei of N, O, C and H to emit characteristic rays to determine the content and spatial distribution of the above elements. The SERS is a commonly used method of trace detection based on the samples after surface modification, can make the material with Raman active detection has been a sharp increase, and then to test, but these technologies need a lot of expensive instruments, process trival, and these can't rapid on-site real-time testing instrument.

Surface acoustic wave (SAW) devices are characterized by simple and convenient signal processing. Interdigital transducer (IDT), a special structure, is adopted to stimulate and transform signals. The SAW devices successfully introduce or extract signals arbitrarily during the propagation[4-6]. Surface acoustic wave devices adopt

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semiconductor planar process, so they are suitable for mass production. In the process of application, the surface acoustic wave device industry shows excellent substitutability. The device has stable performance and good repeatability. SAW devices have been realizing miniaturization, lightweight and power saving, and have been widely used in biosensors[7], toxic gas detection[8], and PH detection of different solutions[9], with strong radiation resistance and large dynamic range. Therefore, rapid detection of TNT using surface acoustic wave devices is a potential detection method, Chen Zhe et al from Hunan University used ultra-high frequency SAW for TNT detection[10], but the manufacturing cost of UHF device is expensive and the process is complex, it is not convenient for mass production. Chen et al conducted a simulation by using COMSOL, which further verified that the devices has great potential as a detection TNT[11].

In order to detect the content of TNT quickly in battlefield water environment and judge the safety of water source, we use surface acoustic wave technology to detect TNT at different concentrations. A surface acoustic wave device with gold electrode was fabricated and modified by cysteine to capture TNT molecules. Based on the mass loading effect of SAW devices, the frequency variation of devices will be caused when TNT molecules are captured. In this paper, a gold electrode surface acoustic wave device is fabricated on piezoelectric materials by using mature ultraviolet lithography. TNT was detected after modifying the gold electrode, and the results were analyzed and discussed.

To selectively detect TNT, we modified the surface of the gold electrode with cysteine (10^{-4} mol/L). The device was soaked in cysteine and refrigerated for 12 h.

A photolitic process was carried out on the purchased Y-128° lithium niobate (Hefei Crystal) substrate, and then a 45-nm-thick gold film was plated by the electron beam coplier. Before the gold plating, a 5-nm-thick chromium layer was needed to increase the adhesion of the gold layer. Lift off process was adopted after the wafers were taken out from the coplier to peel off the gold electrode and the gold pad. A double-ended surface acoustic wave device with wavelength of 12 μm, logarithm of IDT as 50 and aperture as 200 times of wavelength was fabricated.

Ceyear3656D vector network analyzer was used for testing.

UV exposure was carried out on the cleaned lithium niobate substrate (Fig.1(b)). AZ5214 adhesive with positive and negative photoresist properties was used for UV lithography, with a uniform rotation speed of 600 r/min, 6 s, 4 000 r/min, and 30 s. SUSS MA/BA6 exposure machine was used for exposure. After lithography gold-plated, gold-plated after left-off technology is adopted to improve the strip (Fig.1(c, d)), put the lithium niobate films in the beaker, import acetone, and then put the acetone in hot plate temperature is 70 °C, the observed near lithium niobate films have obvious bubbles rise after the beaker into the ultrasonic cleaning machine with 40 kHz frequency ultrasonic 1 min. Rinse with anhydrous ethanol and blow dry with rubber ear balls. Drops of TNT solution of different concentrations were added to the modified SAW devices (Fig.1(e)), and tested after soaking for one hour (Fig.1(f)). The overall experimental process is shown in Fig.1.

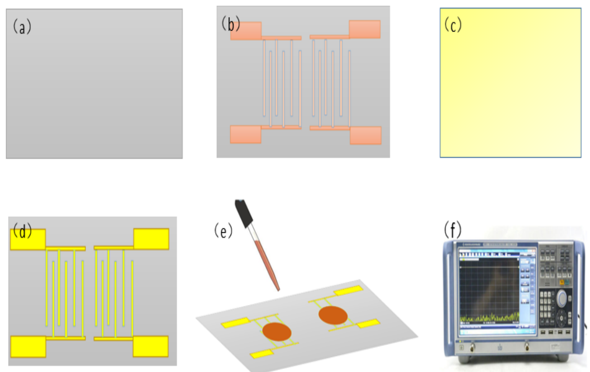

Fig.1 Schematic diagram of fabrication of SAW sensors and the process of detecting TNT: (a) Cleaning lithium niobate; (b) Photoetching; (c) Gold plated film; (d) IDTs obtained by stripping; (e) Electrode modified with cysteine; (f) Test performed using a netword vector analyzer

The same materials and process parameters were used in the fabrication of these devices. The resulting electrode can be seen under the microscope, as shown in Fig.2. It can be seen that the fork finger is uniform and has a good line width.

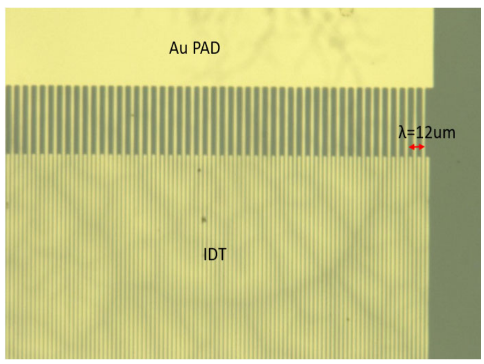

Fig.2 High resolution microscope image of IDTs (The IDT is 3 μm wide and evenly distributed.)

By testing the produced SAW devices, at room temperature, turn on the network vector analyzer, install the probe, and stick the probe to the electrode of the device for measurement. It was found that the performance of the fabricated devices was merely the same and the center frequency was around 325 MHz. The test results were shown in Fig.3.

IDTs are mainly used to excite and detect surface acoustic waves on the surface of piezoelectric substrates, so as to realize the conversion between electrical signals and surface acoustic signals. The mass loading effect and second-order effect of electrodes have a great influence on the propagation characteristics of surface acoustic waves. Because the electrode mass loading effect of SAW sensors will cause changes in the central frequency and phase angle of the device, the sensitivity of SAW sensors is usually based on the following formula:

$$\Delta f=\frac{Cf_0^2}{A}\Delta m\ , \qquad (1)$$

where f_0 is the resonant frequency of the surface acoustic wave device, Δf is the frequency offset, C is the constant, A is the active surface area, and Δm is the mass load (or variation).

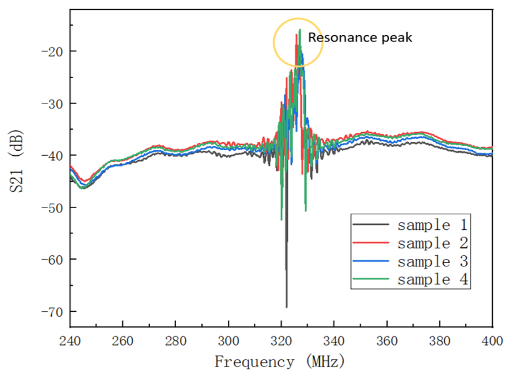

Fig.3 The frequency characteristics of the double-ended SAW sensors

L-cysteine, a common amino acid with special properties, is ubiquitous in living organisms. Its molecular formula is $C_3H_7NO_2S$. It is one of the sulfur-containing -amino acids, which is found in many proteins and glutathione. Cysteine has a sulfur-hydrogen bond (S-H bond) and can form a strong gold-sulfur bond (Au-S bond) with Au^+, which enables gold atoms to interact strongly with cysteine molecules[12]. When the modified gold electrode captures the TNT molecule, the cysteine conjugated gold atoms form the Mersenheimer complex, as shown in Fig.4.

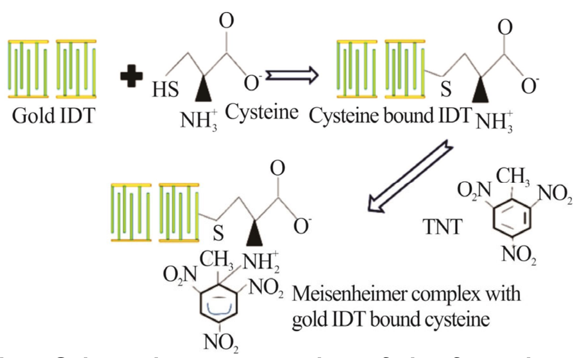

Fig.4 Schematic representation of the formation of Meisenheimer complex between cysteine modified gold nanoparticle and TNT

Drop TNT solution with different solutions to the four samples and test the surface acoustic wave devices after soaking, and the test results are shown in Figs.5—8.

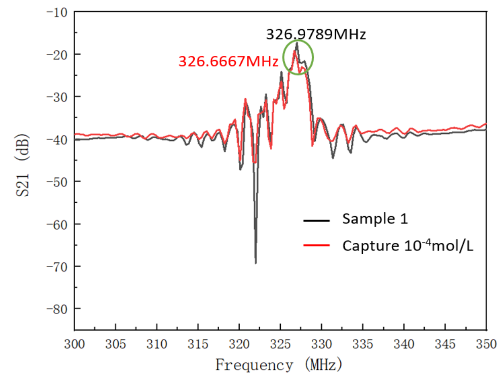

Fig.5 Test results of adding 10^{-4} mol/L TNT to sample 1

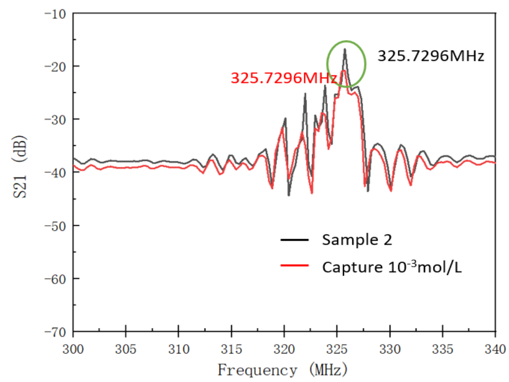

Fig.6 Test results of adding 10^{-3} mol/L TNT to sample 2

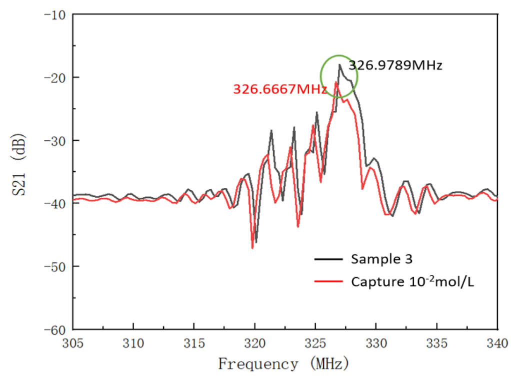

Fig.7 Test results of adding 10^{-2} mol/L TNT to sample 3

It can be seen that the initial frequency of sample 1 and sample 3 is the same as the frequency offset after dropping TNT solution. This is because other substances in the test solution will remain on the device surface after dropping the test solution, causing the device frequency offset. The solubility of TNT detected in sample 4 was the largest, and there were more TNT molecules in the solution, so the frequency change was obvious. The frequency change of sample 1 and sample 3 was 0.312 2 MHz, while the frequency change of sample 4 was 1.249 3 MHz, indicating that the detected TNT molecules caused a change of 0.937 1 MHz in the device.

There is no change in sample frequency after adding two drops of test solution, which may be the result of test solution failure.

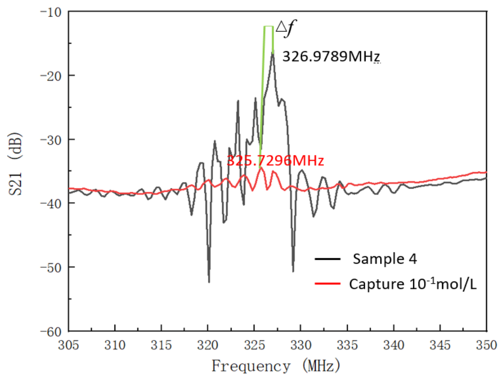

Fig.8 Test results of adding 10^{-1} mol/L TNT to sample 4

Through the above analysis, it can be found that the frequency change of the large-structure gold electrode/lithium niobate SAW sensor is not significant when the concentration of TNT solution is low, but the device has a large frequency shift when the concentration is 10^{-1} mol/L, which proves that the SAW sensor has the potential to detect TNT efficiently and in real time.

In this paper, different concentrations of TNT were tested by making a surface acoustic wave device, which was tested before and after cysteine modification. After capturing TNT molecules, the frequency of the device had a significant drift. The real-time and convenient detection of TNT by surface acoustic wave device reflects the important application value of surface acoustic wave technology in explosive detection and identification, and also enriches the application of surface acoustic wave technology.

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