Study of detecting mechanism of carbon nanotubes gas sensor based on multi-stable stochastic resonance model

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Keywords: carbon nanotubes gas sensor, detecting mechanism, gas ionizing, multi-stable stochastic resonance, numerical stimulation

The detecting mechanism of carbon nanotubes gas sensor based on multi-stable stochastic resonance (MSR) model was studied in this paper. A numerically stimulating model based on MSR was established. And gas-ionizing experiment by adding electronic white noise to induce 1.65 MHz periodic component in the carbon nanotubes gas sensor was performed. It was found that the signal-to-noise ratio (SNR) spectrum displayed 2 maximal values, which accorded to the change of the broken-line potential function. The experimental results of gas-ionizing experiment demonstrated that periodic component of 1.65 MHz had multiple MSR phenomena, which was in accordance with the numerical stimulation results. In this way, the numerical stimulation method provides an innovative method for the detecting mechanism research of carbon nanotubes gas sensor.

Introduction

In signal measurement occasions, it is difficult to extract eigen values of weak signals from a complex background noise system.1-3 MSR, a novel non-linear dynamic model, was proposed by Benzi for the explanation for Earth climate periodic changes in 1980s.4-5 In a non-linear dynamic system, weak signals can be significantly amplified by adding external noise to a MSR system.6-8 MSR has been a useful data processing technique and is widely applied in many research fields such as physics,9-11 medicinals,12,13 biochemistry,14,15 chemical physics,16,17 etc.

Lin et al. first reported the phenomenon of the output SNR in a magnetized plasma system.18 And this method was widely applied to solve some fuzzy problems, such as fault diagnosis,6,7,19 weak signal detection,7,20 etc. Hui, Wang, Mo and Zhang (2012) built a rapid quality predictive model about grass carp using electronic nose combined with MSR SNR analysis.21 Liu, Han, Cai, Jin and Hui (2015) proposed a rapid determination method for Penaeus orientalis prawn freshness based on electronic nose and non-linear MSR technique, and built the relationship between the physical/chemical indexes and double-layered cascaded serial stochastic resonance (DCSSR) by multi-variables regressions (MVR).22 Jin, Zheng, Ge, Deng, Liu and Hui (2015) realized qualitative discrimination for glucose, D-fructose, and sucrose using non-linear SNR spectrum.23 Jin, Ge, Zheng, Cai, Liu and Hui (2015) provided a novel discriminating method for sweetener species by non-linear MSR technique.24 However, little information about the study of detecting mechanism of carbon nanotubes gas sensor based on MSR model was reported.

In this study, the detecting mechanism of carbon nanotubes gas sensor was studied using non-linear MSR model. Numerical stimulation based on MSR was carried out. Meanwhile, gas-ionizing experiment by adding Gaussian white noise with different intensities to the carbon nanotubes gas sensor was performed.

Results and discussion

Numerical stimulation result

The developed numerical stimulation model is displayed in Figure 1A. Electrical potential periodically changes with the change of \( x \). Potential wells appear at the position of \( x \) about \(-3\), \(-1\) and \(3\), respectively. And this model provides theoretical support for following SNR spectrum analysis.

SNR spectrum analysis results calculated by MSR as a function of noise intensity are displayed in Figure 1B. SNR values range from \(-786\) dB to \(-781\) dB, and change with the increase of noise intensity. SNR value begins with \(-878\) dB at the noise intensity of near 2. Two maximal peak values appear at the noise intensity of 2.5 and 6, respectively. After that, SNR value decreases with increase of noise intensity. When modulated by white noise, the first MSR phenomena occurs between the potential well 1 and the potential well 2, leading to the formation of the first SNR eigen peak. With the increase of noise intensity, the transition probability of Brownian particle from the potential...
well 2 to the potential well 3 rises. However, the SNR value rapidly declines due to the status change of the first MSR. With the increase of noise intensity, particle requires adequate energy to move between the 3 potential wells, which leads to the results of SNR spectrum increase. When the noise intensity rises to some extent, the movement period of Brownian particle equals to the driving cycle, and thereby the second SNR eigen peak emerges. SNR spectrum analysis agreed with the numerical stimulation model well. The numerical stimulation results gave a reasonable explanation for the MSR phenomena of gas ionization sensor.

Experimental detection result
The Fourier transform (FT) frequency spectrum recorded by the oscilloscope under different noise intensities is displayed in Figure 2. When the noise intensity is close to zero, the current in the system change a little. And it a periodic component near 1.63 MHz in the frequency spectrum and a small SNR value (see Fig. 2A) can be observed. When the noise intensity reaches 9.2V, the periodic component significantly increases and the SNR value improves. And fragmentary discharge pulses appear due to the improved current (see Fig. 2B). When the noise intensity reaches 12V, the component significantly declines and the SNR value decreases (see Fig. 2C). When the noise intensity reaches 15.4V, a totally different phenomenon occurs (see Fig. 2D). The eigen component improves and the SNR spectrum increases.

The formatting mechanism of 1.63 MHz periodic component is not clear yet. But we could give a possible explanation based on the analysis of gas ionizing characteristics. Gas ionizing is one of the most important research areas in non-linear dynamic research, and DC discharge plasma plays an important role. According to the gas ionizing theory, the self-sustaining dark discharge area is close to the front glow discharge area. The experiment system is in the self-sustaining dark discharge area, so some fragmentary discharge pulses can be observed. By adding external noise, the system enters into the front glow discharge area and electrode pads are in a stable condition, which is similar to non-linear DC discharge plasma. Compared to ions, the electron in the plasma keeps a stable non-thermal status. The ions with positive charges and the electrons with negative charges in the plasma are of high density and in a continuous motion status. The positive and negative charges produced by gas ionizing generate, and their escaping rates are equal. This phenomenon makes the plasma to be electric neutrality. Plasma vibration is a collective motion formed by the interactions of the particles. The plasma frequencies of electrons and ions represent their highest frequency inducing collective motion, which can be calculated as following:

\[ \omega_p/2\pi = \sqrt{e^2n_o/4\pi^2\varepsilon_0m_e} \]  
\[ \omega_{pi}/2\pi = \sqrt{e^2n_o/4\pi^2\varepsilon_0m_i} \]  

Where, \( n_o \) is the plasma density, \( \varepsilon_0 \) is the dielectric constant in the vacuum environment, \( m_e \) is the electric mass, \( m_i \) is the ion mass. The particle concentration in glow discharge area is about \( 10^{16} \text{ m}^{-3} \). So we compare the ion oscillation frequency under the same condition. The ion oscillation frequency of argon, nitrogen, neon and helium are calculated and obtained as near 3.2 MHz, 1.91 MHz, 2.3 MHz, and 1.1 MHz, respectively. In gas ionizing experiment, we conclude that the oscillation is due to the complex components in carbon nanotubes gas sensor, and subsequently forms 1.63 MHz periodic component.

In this research, numerical stimulation about MSR was performed. And gas-ionizing experiment was conducted to validate the stimulating results of numerical model. The results suggested that the experimental results accorded with the numerical stimulating results well.

Materials and methods

Devices and chemical regents
Agilent digital oscilloscope was purchased from American Agilent Company. Polipower alternating current power supply was purchased from Denmark. QJ6005 cocurrent stable supply
was purchased from Hongcheng Electronic Technology Co. Ltd., (Suzhou, China). Automatic digital multimeter was purchased from Shenzhen Victory Advanced Electronic Technology Co. Ltd., (Shenzhen, China). High pure (99.999%) aluminum plate was purchased from Shanghai Special material Co. Ltd., (Shanghai, China). Continuously adjusted high pressure cocurrent supply (0-800V) and carbon nantube growth furnace were self-made in our lab. Cobaltous sulfate (analytically pure) was purchased from Zhejiang Yixing Chemical Reagent Co. Ltd., (Yixing, Zhejiang). Deionized water was used in the experiment.

Preparation of carbon nanotubes gas sensor

High pure (99.999%) aluminum plate was ultrasonic cleaned in the mixture solution of acetone and ethanol (1:1) for 30 min. After that, it was polished in the mixture solution of ethanol and perchloric acid for 10 min and using deionized water to wash. Then put it to 0.3 mol/L oxalic acid solution and use current supply (40 V) to oxidize it in the positive pole for an hour. Later, place it to the 5% phosphoric acid and chamber it under 50°C for 15 min. The size, gap and depth of the pore was 60 nm, 100 nm and 2 μm, respectively. Thus the anodic aluminum oxide (AAO) formwork was completed.

Then, using alternating current power supply to deposit cobalt particles (the size was near 60 nm) under the AAO formwork in the mixture solution of 60 g/L cobaltous sulfate and 25 g/L boric acid. After that, the AAO formwork was placed into the carbon nanotubes growth furnace. When it reached to 645°C, an airflow of acetylene and hydrogen (1:2, V/V) was introduced for 5–10 min. After cooling to the room temperature, it was taken with the protection of nitrogen.

The carbon nanotubes gas sensor consists of 2 poles. Carbon nanotubes electrode was used as the positive pole (see Fig. 3), and aluminum plate was used as the negative pole. The carbon nanotubes electrode was packaged with insulating membrane material. And the membrane packaging gas detection part was cut to expose the carbon nanotubes. And then the aluminum plate was used to package the membrane. So, the detection part of carbon nanotubes corresponds to the negative pole, which effectively controls the gap between the 2 poles.

Detection system

The schematic structure of gas ionizing experimental system is displayed in Figure 4. It consists of 2 main parts: carbon nanotubes gas ionizing device and electronic signal acquiring device. Carbon nanotubes gas sensor was put in an airtight detecting air chamber, where $R = 100 \text{ K}$, $R_1 = 1 \text{ K}$. Change in the voltage of the electrode induces the change of electronic signal in the oscilloscope, which realizes the parameter measurements due to gas ionizing phenomena.

MSR

MSR is a typical non-linear model and proposed by Benzi for the explanation for Earth climate periodic changes.1,25,26 MSR phenomenon has 3 elements: a bistable system, a coherent input, and a noise source,1 which can be described as

$$\frac{dx}{dt} = -\frac{dV(x)}{dx} + A \sin(2\pi ft + \psi) + MI(t) + D\xi(t) \quad (3)$$

Where $x$ is the position of the Brownian particle, $t$ is the time, $A$ is periodical signal intensity, $f$ is signal frequency. $D$ is external noise intensity. $M$ and $D$ are adjustable parameters, $I(t) = CN(t) + N(t)$ denotes carbon nanotubes sensor signal $CN(t)$ and intrinsic noise $N(t)$, $\xi(t)$ is the external noise, and $V(x)$ is the simplest double-well potential with the constants $a$ and $b$ characterizing the system. Noise intensity is a parameter of MSR model. MSR model is used as a data processing method in

![Figure 2. Frequency spectrum in different noise intensity of (A) zero; (B) 8.5V; (C) 11.7V; (D) 14.3V.](image-url)

![Figure 3. Structure of carbon nanotube electrode.](image-url)
SNR is the common quantifier for MSR and it can be approximated that the weak signal can be detected from noise background. The intensity of signals will increase, which makes it possible to surmount the energy barrier and enter another potential well. The minima of $V(x)$ are located at $\pm x_m$, where $x_m = (a/b)^{1/2}$. A potential barrier separates the minima with the height given by $\Delta U = a^2/4b$. The barrier top is located at $x_0 = 0$. When three elements of MSR interact coherently, the potential barrier can be reduced and the Brownian particle may surmount the energy barrier and enter another potential well. The intensity of signals will increase, which makes it possible that the weak signal can be detected from noise background. SNR is the common quantifier for MSR and it can be approximated described as:

$$\text{SNR} = \sqrt{2\Delta U} \left( \frac{A}{D} \right)^2 e^{-\Delta U/D}. \quad (6)$$

**Numerical stimulation**

According to the MSR combined with multi-stable characteristics in the dynamic system, Eq. (7) is used to performed numerical stimulation.

$$\frac{dx(t)}{dt} = - \frac{dV(x)}{dx} + A_0 \cos(\omega t + \varphi) + \xi(t) \quad (7)$$

Where, $\xi(t)$ is the Gaussian white noise, $V(x)$ is the potential function, $x$ is the position of the Brownian particle, $t$ is the time, $A_0$ is periodical signal intensity.

**Conclusions**

In this paper, the detecting mechanism of carbon nanotubes gas sensor utilizing non-linear MSR model was studied. Numerical stimulation based on MSR was performed, and SNR value was calculated. Gas-ionizing experiment by adding external white noise induced 1.63 MHz periodic component in spectrum area. The numerical stimulation results demonstrated that 2 maximal SNR values appeared in the SNR spectrum, which explained the change of the potential fluctuation. In addition, the results of gas-ionizing experiment indicated that 1.63 MHz periodic component in the frequency spectrum had MSR phenomena under different noise intensity, which accorded with the numerical stimulation results well. Therefore, the numerical stimulation method successfully explained the detection mechanism of carbon nanotubes gas sensor. And this method provides a novel way for carbon nanotubes sensor detecting mechanism research.

**Disclosure of Potential Conflicts of Interest**

No potential conflicts of interest were disclosed.

**Funding**

This work is financially supported by Zhejiang Provincial Natural Science Foundation (Grant No. Y107003).

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