PALLADIUM NANOPARTCLE COATED TOBACCO MOASIC VIRUS SENSING LAYER BASED SURFACE ACOUSTIC WAVE HYDROGEN SENSORS

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ABSTRACT

We describe ongoing research aimed at investigating the role of engineered nanomaterials in designing SAW resonator based gas sensors. We investigated the use of Pd-cluster coated, engineered tobacco mosaic virus as sensing material for the development of hydrogen sensors using 315 MHz surface acoustic wave (SAW) two-port resonators. Absorption and desorption of hydrogen from the sensing layer causes the SAW devices to be perturbed. This perturbation results in variation of wave velocity and hence resonant frequency of the device that can be calibrated to determine the concentration of hydrogen. The sensor showed repeatable performance when tested over a range of concentration from (0.2-2.5%) hydrogen with low response times (30sec). High robustness and stability of film was observed when tested continuously over a range of concentrations and long durations. The sensor was seen to respond by producing a hydrogen concentration independent increase in frequency opposite to the more common mass loading behavior characterized by decreases in frequency.

KEY WORDS

Surface Acoustic Wave resonator, Hydrogen Gas Sensor, Nanocrystalline, Tobacco Mosaic Virus

INTRODUCTION

Bio-nanotechnology is aimed at design and synthesis of novel biological materials. These materials could be used to design optical, biomedical and electronic devices. One such example of nanoscale biological system is a virus. Viruses have been given a lot of attention for assembly of nanoelectronic materials. Tobacco Mosaic Virus (TMV) is a well-known plant virus contagious to tobacco leaves. TMV has a 300 nm long tubular structure with an outer diameter of 18 nm and an axial canal 4 nm in diameter. Strains of this virus have been previously coated with metals, silica or semiconductor materials and formed end-to-end nano-rod assemblies [1, 2]. In this work, the Pd-cluster coated, engineered TMV particles were studied for hydrogen gas detection with the help of Surface Acoustic Wave (SAW) resonators.

SAW RESONATOR AND THEORY

Saw resonators used here are two-port devices consisting of input interdigital transducers (IDT), output IDTs and reflection gratings. These IDT are constructed on piezoelectric material such as quartz, lithium niobate or lithium tantalite. The application of electrical voltage across a piezoelectric material causes the material to get deformed producing acoustic waves. The application of electrical signal across the input IDT converts the applied signal to mechanical acoustic waves. These waves travel across the surface towards the output IDT. The output IDT converts these mechanical SAW vibrations back to electrical voltage. Presence of a sensing layer on the substrate causes the acoustic wave velocity to be affected. Absorption of the target analyte by this sensing film causes further change in the wave velocity. These changes in wave velocity are directly related to changes in frequency given by equation 1 [3, 4] where the wavelength of the device is fixed by geometry of the device.

$$f_o = \frac{v_o}{\lambda} \tag{1}$$

Where
f_o is resonant frequency
v_o is acoustic wave propagation velocity
λ is wavelength

The SAW device is highly sensitive to perturbations arising from many different mechanisms such as changes in mass density, elastic stiffness coefficients, dielectric property of film, and electric conductivity [4] which causes the variation in saw wave velocity v_o. This variation produces a phase shift between the applied and the received signals thus causing the frequency of minimum impedance to be shifted away from the resonant frequency f_o. These fractional changes in wave velocity are tracked by fractional changes in frequency or phase [9] by placing the device in an oscillator loop (Figure 1). The relation between the phase, frequency, and acoustic velocity is given by equation 2

$$\frac{\Delta v}{v_o} = \frac{\Delta f}{f} = \frac{\Delta \varphi}{\varphi} \tag{2}$$

EXPERIMENTAL SETUP

This SAW device was connected on a printed circuit board with connections to and from the board made with help of SMA connectors. The resonator mounted on the PCB was placed in a stainless steel cell through a small opening on the top to be in continuous contact with the incoming gas. It was ensured that the seal was leak proof. To investigate the gas sensing properties of the sensing

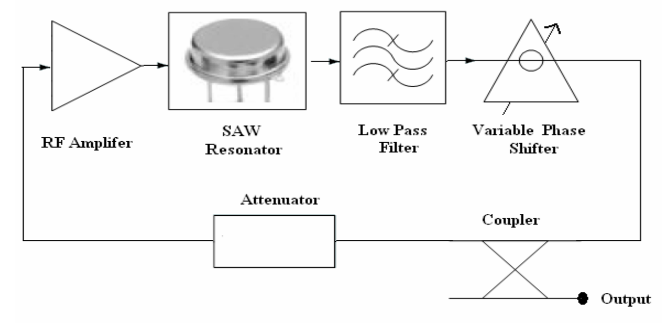

Figure 1. Block diagram of the oscillator

layer, an in-house, fully automated gas dilution system was used [5]. The cell was connected in series with the output of 4 MKS type 1479A mass flow controllers connected to a 4-channel MKS type 247 readout. These MFCs were used to produce a wide range of gas concentrations from pure to ppm range with nitrogen used as both diluting and reference gas. The flow rate was kept constant at 1000 sccm to prevent any flow related effects, with operating temperature fixed at 22.5 ºC. The gas dilution setup is shown in Figure 2.

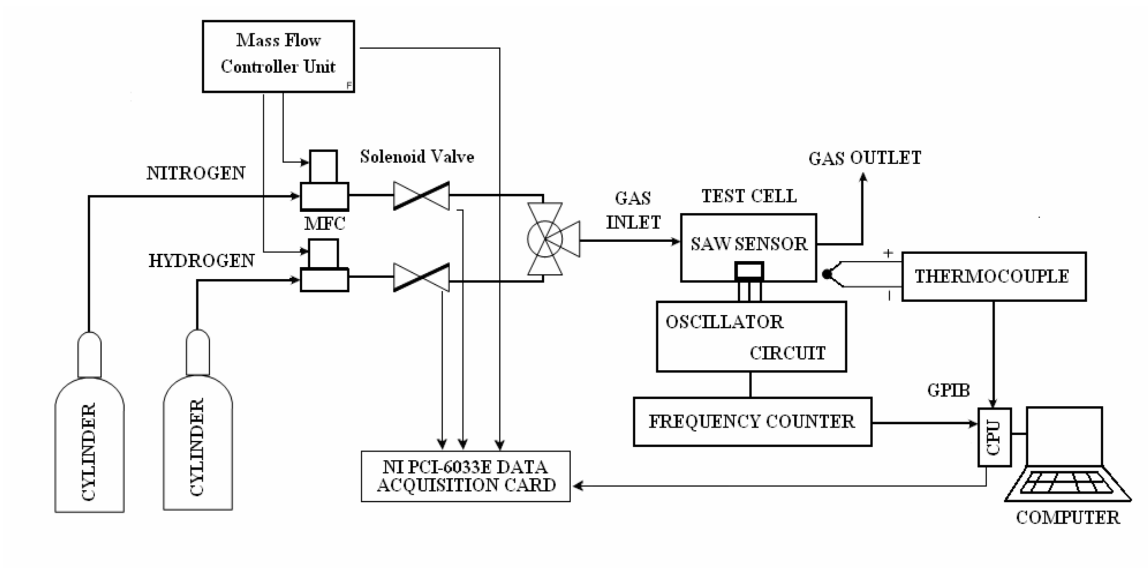

Figure 2. The experimental setup of gas-dilution and RF test system

LAYER PREPERATION

The RP1239, 315 MHz, TO-39 package was uncapped and sputter coated with 1000 Å of SiO_2. SiO_2 was used both as an insulating and guiding layer. The use of insulating layer is to prevent the shorting of IDTs due to coating of conducting film on its surface. The resonator was later drop coated with a 20 µL sample of 0.01 mg/mL Pd-TMV solution. Synthesis of Pd-TMV has been described previously [1]. The coating of SiO_2 and Pd-TMV particles resulted in changes of both attenuation and frequency which were measured using an Agilent 8753ES S-parameter Network Analyzer and have been tabulated in Table 1. The uncoated device resonant frequency and attenuation were measured as 315.028750 MHz and -3.5755 dBm.

TABLE 1. SAW RESONATOR FREQUENCY AND ATTENUATION MEASUREMENTS FOR THE PD-TMV RESONATOR

Process	Frequency change	Attenuation change
1000 Å of SiO_2	0.65625 MHz	-7.725 db
20µl Pd-TMV coating	0.05250 MHz	-5.907 db

RESULTS

Frequency shifts for the Pd-TMV coated resonator when exposed to hydrogen in the 0.2-2.5 volume% range are shown in Figure 3. Form the figure it is seen that the sensing film responds by producing an increase in frequency to hydrogen challenges. The behavior is contrary to mass loading wherein decrease in frequency takes place by analyte absorption. This behavior may be explained by the acousto-electric response mechanism marked by producing an increase in frequency. When a SAW propagates in the piezoelectric surface it produces a layer of bound charges. The deposition of a conductive film on the surface causes the redistribution of charge carriers. This redistribution compensates the layer of the bound charges developed due to the passing surface wave [9].

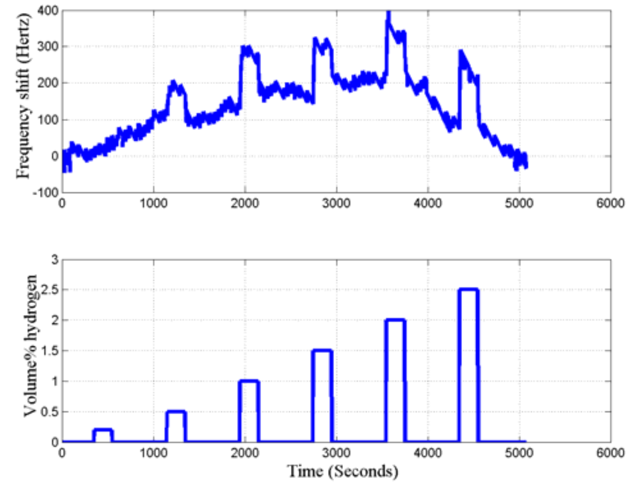

Figure 3. The response of Pd coated TMV to 0.2-2.5 % hydrogen

It was observed that the absorption and desorption of hydrogen from the sensing films was reversible. Repeatability was also observed over weeks of testing. The film did not show any signs of degradation or peeling from continuous testing over range of concentration and long durations. The response times for nearly complete (99%) response of the device were found to be around 30 sec for the range of concentrations from 0.5-2.5 volume% hydrogen in nitrogen as seen from Figure 4. These films responded immediately and showed no sign of aging which are typically seen in pure Pd films when not exposed to hydrogen for few days [6].

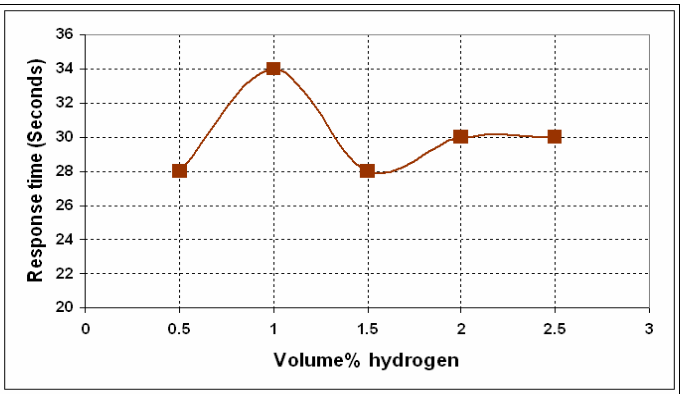

Figure 4. The response times for Pd coated TMV resonator in response to 0.2-2.5 % hydrogen

DISCUSSION

In this paper, 2.3 nm Pd nano-particle coated TMV sensing films on SAW resonators have been investigated for detection of hydrogen at room temperature. Frequency increases were observed upon hydrogen challenges, which is unexpected and typically associated with an electro-acoustic response mechanism. The responses were immediate and did not require activation cycling before giving full responses. Sensor responses were reversible, and showed repeatable performance and robustness after weeks of testing. The Pd-TMV sensing film produced easily measurable responses with fast response and recovery times for nearly full response. Future work involves characterizing the behavior of the nonomaterial film in detail.

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