Engineering silver nanostructures for surface acoustic wave humidity sensors sensitivity enhancement

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Abstract: In this paper, the sensitivity of the LiNbO\textsubscript{3} surface acoustic wave (SAW) based humidity sensors has been enhanced with various nanostructured Ag materials, including thermally evaporated or chemically synthesized, and then thermally annealed ones. The results showed that the humidity sensitivity of the SAW devices increases with the surface roughness (porosity) of the film, and can be further improved when Ag NPs are used. Smooth Ag film deposited by evaporation onto the SAW devices did not change the humidity sensitivity noticeably, but those with chemically deposited high porosity Ag films have a good sensitivity of 80 kHz/75\%RH. The SAW sensors with the Ag NPs have the highest sensitivity up to about 800 kHz/75\%RH, at least one order of magnitude higher than that reported before. The SAW sensors with Ag nano-particles showed a strong non-linearity, and explained by the different chemisorption capabilities of Ag and LiNbO\textsubscript{3} surface.

Keywords: surface acoustic wave (SAW), humidity sensors, silver nanoparticles

1. Introduction

Monitoring and controlling of humidity are essential for many applications such as weather forecast, environmental controls for laboratories and product lines in industries.\textsuperscript{1,2,3} There have been numerous studies to develop various humidity sensing technologies and associated systems, and some of them have been commercialized. Most of the humidity sensors rely on
the changes of electrical conductivity, impedance or capacitance of the devices upon absorption/desorption of water molecules when the humidity changes. Polymeric materials or porous ceramics have been widely used to enhance the performance of the humidity sensors as they increase the capability of absorbing water molecules either through their specific material properties or significantly increased surface areas.

One of the distinctive features of nanomaterials is their extremely large surface to bulk ratio. This has been effectively utilized for various applications where the surface area is an important or a dominant factor such as in catalytic reaction, solar cells, sensors etc. Therefore, metal or oxide nanomaterials are potentially attractive for the development of high performance sensors for humidity, gas, chemical and biological sensing. Among all the metals and oxides, silver (Ag) nanoparticles have received particular attentions for humidity sensors owing to its strong capability to attract water molecules. It was reported that resistive humidity sensors made from glass ceramics containing Ag nanoparticles (NPs) and optical fibre humidity sensors with embedded Ag NPs in polyaniline have significantly improved sensitivities.

Nanostructured metal and oxide materials can be synthesized by various methods. Physical deposition methods such as thermal evaporation and sputtering have been used to deposit various materials, mostly in thin film form with smooth surface, unless some special technique applied, such as ion beam assistance. Smooth and dense films are not particularly useful for humidity sensing applications. Chemical synthesis is one of the most popular methods with advantages of low cost, robustness, and is suitable for most of metal NPs synthesis with various shapes and sizes. The surface morphology and chemistry of the metal colloids in the chemical solutions are important factors for controlling the shape and size of the nanoparticles. The states of chemical decomposition such as –NH₂ group employed by coupling agents on the surface of NPs can be modified to control the capability of water adsorption, a common chemisorption process through the hydroxyl bonding. Smith et al reported that Ag NPs with controlled sizes and shapes can be simply synthesized by chemical reaction of silver nitrate and glucose, the so-called Mirror reaction process. Depending on the process, most of chemically-synthesized nanomaterials are actually not discrete nanostructures, but uniform films with high porosity, thus a subsequent annealing is often used to transfer the film-type materials into discrete NPs. Post-synthesis annealing is also used to decompose residual carbons and other organic residuals on the surfaces of films or NPs, particularly useful for sensing applications.
Surface acoustic wave (SAW) resonators are a type of sensors with high sensitivity to changes occurred on/in the surface, including temperature, humidity, mass loading, electrical field etc and have been intensively explored for the development of gas, temperature, humidity and biochemical sensors etc. SAW humidity sensors, mostly based on mass loading effect, are simple in structure, low cost, easy to use, and have high sensitivity. Nanomaterials such as ZnO nanorods have been used for the development of SAW humidity sensors, demonstrated much enhanced sensitivities. Although Ag NPs are proven to be one of the best nanomaterials for the development of high sensitivity humidity sensors, it has not been utilized for SAW-based humidity sensors yet. In this work, we report the development of SAW humidity sensors with incorporated Ag NPs. Results showed that the sensitivity of the SAW sensors is strongly dependent on the porosity of the Ag layer or the number and the sizes of Ag nanoparticles on the surface. Ag films with high porosity are good for humidity sensors. SAW devices with incorporated discrete Ag NPs of the density of about 4.7x10^6 cm^-2 showed 400 times improvement in sensitivity compared with that with a smooth evaporated Ag film.

2. Experimental Methods

2.1 Device Design and Fabrication

SAW humidity sensors were fabricated on 128° Y-cut lithium niobate (LiNbO₃) substrates which has an acoustic velocity of 3980 m/s and electromechanical coupling coefficient of k²=4.8%². Two-port interdigitated transducers (IDTs) with a gold layer of about 100 nm thickness were fabricated on the LiNbO₃ substrate using the conventional photolithography and lift-off process. The IDT electrodes consist of 60 pairs of fingers with a spatial periodicity of 32 µm, i.e. the wavelength, λ. The resonance frequency of the device is related to the phase velocity by the equation, v = fₐλ, and it is ~124 MHz. The distance between the two IDTs is 5 mm, on which Ag film or Ag NPs will be deposited and synthesized for humidity sensing experiments.

2.2 Preparation of silver films

Thin silver films or NPs were deposited by either thermal evaporation or chemical reduction of silver nitrate (AgNO₃) by glucose. In order to deposit Ag film or NPs on the wave path
of the SAW devices without contaminating or destroying the IDT electrodes, a photoresist was used to coat the IDTs before evaporation or chemical synthesis.

Thermal evaporation was conducted at a base chamber pressure of $2 \times 10^{-6}$ Torr, Ag was evaporated with a thickness of 20 nm. Sodium hydroxide (NaOH), aqueous ammonia (NH$_3$) and glucose were purchased from Sigma. Methanol and silver nitrate were obtained from Fisher Scientific. All chemical regents were used in the experiments as purchased without further purification. The glassware were thoroughly cleaned and rinsed with DI water. The chemical processing is as follows: a 4.8 mL aqueous solution of 0.05 mol/L NaOH was added into a 120 mL aqueous solution containing 0.047 mol/L silver nitrate until a brownish precipitate of Ag$_2$O was formed. A 3.5 mol/L ammonia solution was then added into the mixture under vigorous stirring until the tint solution became transparent, i.e., forming [Ag(NH$_3$)$_2$]$^+$. Another 0.8 mL silver nitrate solution of 0.35 mol/L was then added into the solution, and followed by adding a 154.5 µL of 3.5 mol/L ammonia. The reductant included a 80 mL of 1.9 mol/L glucose combined with a 40 mL methanol. Finally the [Ag(NH$_3$)$_2$]$^+$ containing solution and the reductant were mixed at 35 °C in a water-bath. The LiNbO$_3$ SAW devices were then directly immersed into the solution, and the Ag film was deposited on the required areas of the SAW devices. Film thickness, porosity and size of the nanoparticles were controlled by the synthesis time of 2, 4 and 6 min and their effects on the performance of the SAW humidity sensors were studied.

2.3 Nanoparticle formation by annealing

To form discrete Ag nanoparticles for better sensing applications, the Ag films on the SAW devices were subjected to post-synthesis annealing, so that the Ag element can aggregate together to form nanoparticles. After vigorous cleaning in solvents and DI water, the SAW devices with Ag thin films were annealed in N$_2$ atmosphere in a furnace, with the annealing temperature and duration varied from 200 to 500 °C, and 10 to 150 min, respectively. It was found that those annealed at 400 °C for one hour have formed discrete Ag nanoparticles with a good distribution and sizes, suitable for the sensor applications. 400 °C was then used for annealing the samples.

2.4 Characterization and sensing experiments

Transmission properties of the SAW devices and humidity sensing were investigated using a network analyser (Agilent E5071C). The resonant frequency and phase angle were
automatically recorded with the time using a LabVIEW (National Instrument) based program. For humidity sensing experiments, the SAW devices mounted on a PCB board was sealed in a metallic isolation chamber (the dimensions of chamber LxWxd is 100x80x20 mm), fitted with SMA adapters and coaxial cables. Figure 1 shows the schematic drawing of the measurement set-up. The gas inlet and outlet were connected to the chamber with a commercial hygrometer (Thermo Hygrometer TASI 621) fixed at the outlet of the chamber to monitor the humidity. The humidity was adjusted by varying the flow ratio of dry N₂ to wetted N₂ (but keeping the total flow rate constant) through a bottle containing water. Both of the gas flows were independently controlled by mass-flow controllers (Sevenstar CS200A). All sensing experiments were conducted at room temperature with a temperature fluctuation less than 1 °C. Microstructure of the silver films and nanoparticles on SAW device surfaces was characterized using a scanning electron microscope (SEM, Hitachi S-4100). The average nanoparticle size was measured and analysed using Image Analysis Tool Version 3.0 and Adobe Illustrator CS4. The optical property of the films was measured on a M501 UV–Vis–IR spectrophotometer.

3. Results and discussions

3.1 Morphology and microstructure

It is well known that film morphology and nanoparticle size are important factors influencing the sensitivity of humidity sensors,¹⁴ therefore, in order to clarify these effects on the LiNbO₃ SAW devices, the surface morphology and microstructures of the synthesized Ag films and NPs under different conditions have been characterised. The surface of the Ag thin films deposited by thermal evaporation is smooth with mirror-like appearance. In contrast, the films deposited by chemical synthesis have a rough and porous surface. Figures 2(a) & 2(b) show the SEM images of the samples with the synthesis time of 2 and 6 min respectively. Clearly the porosity of the film decreases with the increase in chemical reaction time. As the reaction time was increased, Ag particles filled up the gaps, leading to Ag films with less pores and gaps. For the sample with 4 min reaction time, the surface morphology is in between the two samples shown in Figs. 2(a)&2(b).

After the Ag films were annealed at the optimal condition of 400 °C for one hour, it was found that a continuous Ag films became spherical nanoparticles with sizes in the range of a few tens of nanometers (nm) to a few hundred of nanometers separated from each other.
When a thin Ag film on the insulator substrate is heated to a certain high temperature, they tend to aggregate together to form NPs, driven by surface tension. The obtained aggregation temperature in this study is in agreement with the observations by Lee et al. Figures 2(c) & 2(d) show the SEM pictures of Ag nanoparticles formed by annealing at 400 °C for the corresponding samples shown in Figs. 2(a) & 2(b). It is clear that the porous Ag films have totally transferred into isolated NPs, distributed evenly on the surface. For sample S4, the Ag film becomes discrete Ag NPs with limited residual Ag material on the surface. For the thicker Ag film of sample S5, the same aggregation process was observed, and the density and size of the NPs increase compared to those of S4. This result is consistent with the results that the mean average diameter increases with the increase in thickness by the chemical methods. The mean diameters of the Ag NPs are 260±30, 300±30, 330±30 nm for samples with the synthesis time of 2, 4 and 6 min respectively, increasing with the reaction duration. The number of nanoparticles for S4 and S5 are 5.4x10⁶ and 4.7x10⁶ cm⁻², respectively, not significantly different from each other. Figure 3 shows the UV-vis spectrum for all the samples. The main noticeable difference between the as-synthesized samples S1-S3 and the annealed samples S4 and S5 is the peak at 360 nm. For S1-S3, there is a little peak shoulder at 360 nm, and it becomes a well-defined peak, much larger than that of S4 after 6 min annealing at 400 °C.

3.2 SAW sensor humidity response

Figure 4 is a typical transmission spectrum and phase spectrum of the LiNbO₃ SAW devices with the deposited Ag NPs. The central frequency is round 123 MHz, in agreement with the design. The SAW devices with various surface morphologies and sizes of the Ag films and NPs were used for humidity sensing and the experimental measurement results are summarized in Table I.

Figure 5 shows the dependency of resonant frequency, phase angle, insertion loss and phase frequency of the SAW device (S5) on time when subjected to a cyclic humidity change from 70% RH to 16% RH. The red triangles are the humidity values measured using a commercial hygrometer. The resonant frequency decreases (or increases) once the humidity was increased (or decreased), and returns to the original value when the humidity was changed back to ~16% RH. The insertion loss decreases by approximately -2 dB, and the phase angle of the SAW device changes by about 18° as shown in Figs. 5(b), 5(c) and 5(d). The frequency did not show good saturation characteristics, different from other observation.
saturation behaviour is believed to be caused by the gas flow configuration of the measurement system, rather than the slow response of the devices.

The humidity effect on the characteristics of a SAW device are mostly attributed to the mass loading and the change of surface capacitance (or conductance). Additional mass loading of water molecules is introduced on the SAW surface when the humidity is increased, leading to frequency change. The existence of water on the surface also damps the acoustic wave, leading to a decrease of the transmission signal, i.e. increase of the insertion loss. The existence of water either in an isolated form (droplets or patches) or in a continuous form will change the capacitance of the surface, affecting the transmission properties of the devices, especially the phase angle and insertion loss of the SAW devices. The relative change, $\Delta \nu$, in original SAW phase velocity, $\nu_0$, is given by following equation,

$$\frac{\Delta \nu}{\nu_0} = -\frac{k^2}{2} \frac{\sigma_s^2}{\sigma_s^2 + (\nu_0 C_s)^2}$$

where $\sigma_s$ is the sheet conductivity of the film, $k^2$ and $C_s$ are the electromechanical coupling coefficient and the surface capacitance of the device. A change of $C_s$ will lead to the change of the phase of the SAW devices. When the critical sheet conductivity is equal to $\sigma_s = \nu_0 C_s$, a peak of $\frac{\Delta \nu}{\nu_0} = -k^2/4$ is observed. Therefore, a change in phase angle can provide a simple and quick method to measure the humidity change as shown in Fig. 5(c). The present work also demonstrated that multiple responses of resonance frequency, insertion loss and phase of a SAW device can be used for humidity sensing, better than the commonly used resonant frequency only sensing method, with better accuracy.

The sensitivity of the SAW devices to humidity was investigated at different humidity levels with the result shown in Fig. 6. A frequency response was measured under a fixed change step of humidity (~14% RH) from 15% to 85% with each measurement lasting for 300 s. The resonant frequency only shifts by 3.1 kHz when the humidity was changed from 15% RH to 28% RH (as shown in the inset of Fig. 6), but decreases by 187 kHz when the humidity was changed from 73% RH to 85% RH, approximately sixty times larger, showing the non-linear response of the device to the humidity change.

Figures 7(a) and (b) show the response of frequency, insertion loss, phase frequency and phase as a function of relative humidity. The responses of all the parameters to the change of humidity are non-linear, and the sensitivity increases with the humidity. Nonlinear behaviour
is often observed for humidity sensors, and the reason is not clear yet. Generally, sensors with uniform polymer layers have a better linearity,\textsuperscript{32} while those using the nanomaterials may have non-linear behaviour.\textsuperscript{33,34} Detailed observation reveals that the response of the frequency shift with humidity can be roughly divided into two linear regions with different gradients. This can be explained by the non-uniform absorption capability of the surfaces of two different materials, i.e. Ag and LiNbO\textsubscript{3}. According to Grotthuss mechanism,\textsuperscript{35} initial water molecules are chemically bonded with the materials, while afterwards, a thin layer of water is formed from the physisorbed water molecules. Material surface with better chemical bonding with water molecular such as hydroxyl group of terminals\textsuperscript{30} are more hydrophilic, and are able to absorb more water, hence the large capability of water absorption. Ag NPs formed by chemical synthesis and post-synthesis annealing have a better chemical bonding with water molecules than the surface of LiNbO\textsubscript{3}, and they are able to attract more water molecules than the LiNbO\textsubscript{3} surface. The initial water absorption takes place possibly only at the surface of the Ag NPs, resulting in the first linear region in Fig. 7(a) at low humidity. With the increase of humidity, a thin layer of water eventually is formed on the whole surface of Ag NPs and LiNbO\textsubscript{3}, and the frequency shift is then proportional to the water accumulated on the whole surface. Therefore, the sensitivity linearly increases with the humidity, as represented by the second linear region.

The gas flow rate was found to influence the sensitivity significantly, especially for the phase angle. A flow rate of 100 sccm was used for the experiments discussed above. Figure 8 shows the phase frequency responses to a periodic change of humidity at different gas flow rates. The results show that the response becomes much quicker when the flow rate was increased, and the response saturates much faster, indicating that it is better to use phase angle to detect the humidity sensing at a higher flow rate.

3.3 Effects of morphology and nanoparticle size

It is well recognized that the morphology of absorption layer will affect the sensitivity of the humidity sensors. Figure 9 is the frequency shift as a function of humidity with synthesis time of the Ag films as a variable. The SAW device (S6) with the evaporated smooth Ag films shows a very limited frequency change with humidity over the measured humidity range, and the total frequency shift is linear but only about ~2 kHz with a humidity change from 10 to 85\%RH. The frequency shifts for all the samples with chemically-synthesized Ag NPs are similar to each other at the humidity level below 50\% RH, however, the discrepancy between
the humidity sensing results increases as the humidity level was increased. The shift of the resonant frequency of the SAW device decreases as the synthesis time for the Ag films increases, which can be divided into two regions with different gradients due to the different chemical bonding capability with water as explained above. As shown by the SEM pictures in Fig. 2, the porosity is higher for sample S1, but decreases with the increase in synthesis time, for sample S2 to S3. Therefore, it clearly shows that a high porosity is beneficial for high sensitivity of the SAW sensors. It should be noted that the total frequency shift of S1 induced by a humidity change from 10 to 85%RH is more than 80 kHz. The results demonstrated the Ag films porosity has a strong effect on the sensitivity of the SAW sensors.

Figure 10 is the comparison of the frequency response of S4 and S5 with Ag NPs formed by annealing to the humidity change from 10 to 85%RH. The sensitivity of S5 is much higher than that of S4, and the frequency shift upon a change of humidity from 10 to 85% RH is ~850 kHz, 4 times larger than that (~207 kHz) of S4, and more than one order of magnitudes larger than those with Ag films (S1-S3) as shown in Fig. 9. As shown in Table 1, the Ag NP size increases from 260 nm to 330 nm for the devices with the films synthesized for 2 and 6 min, respectively. These results therefore indicate that the high sensitivity of the SAW devices is attributed to the high density and larger particle sizes of the Ag NPs formed on the surface by post-synthesis annealing. It is interesting to compare the results from the pair of sample S1 and S3 with those from sample S4 and S5. The as-deposited sample S1 has a large frequency shift than that of S3 owing to the larger porosity of S1 than that of S3. On the other hand, sample S4 and S5 (which are the annealed samples of S1 and S3) show an opposite result, i.e. sample S4 has a much smaller frequency shift than that of S5. The possible reason for the great enhancement of the sensitivity for S4 and S5 is that the heat treatment may contribute to decomposition of residual carbon compounds such as CO, CO2 and H2O, enabling the Ag NPs to absorb more water molecules as compared to the as-deposited Ag films of S1 and S3.

Figure 11 shows the frequency shift as a function of time for the samples with the Ag layers prepared by different methods. The chemical synthesis time was 6 min for both sample S3 and S5, but S5 was annealed to form Ag NPs. Sample S6 has the evaporated dense and smooth Ag film. Compared with a frequency shift of ~2 kHz for sample S6, sample S3 with a high porosity shows a frequency shift of ~45 kHz, while sample S5 shows a shift of ~800 kHz, for the same change range of the humidity. This clearly demonstrates that the sensitivity increases with the increase in roughness or porosity of the Ag layer, as well as the formation of nanostructures. However, it should be pointed out that all the sensors have no saturation
behaviour over time at different humidity levels as shown in Fig. 5 and Fig. 11. No saturation behaviour is quite common for humidity sensors, possibly is related to different absorption mechanisms\textsuperscript{36}.

The stability of S5 was investigated briefly for a period of three days (~8 hrs x3), and the responses of the device to the change of humidity from 16 RH\% to 70\%RH as shown in Fig. 5 was found to remain almost unchanged, indicating its good stability. Detailed work for the long term stability at different humidity levels for different devices is ongoing, and will be reported elsewhere.

Table II is a comparison of the sensitivities of the SAW based humidity sensors reported in this paper and literature. The sensitivities of our SAW devices with the evaporated Ag film is comparable to those in literature without surface treatment, whereas those with chemically deposited high porosity Ag films have much higher sensitivities compared to most of the SAW humidity sensors with ZnO NPs and polymer absorption layer\textsuperscript{5,36}. The SAW devices with the Ag NPs in this study show the highest sensitivity ever reported, clearly demonstrated its superior property.

4. Conclusions

In summary, LiNbO\textsubscript{3} SAW based humidity sensors with incorporated various types of Ag materials have been investigated, including thermally evaporated Ag films, porous Ag films synthesized by Mirror chemical reaction, as well as post-annealed Ag nanoparticles with sizes in the range of 220 to 330 nm and density of $\sim 5\times10^6$ cm\textsuperscript{2}. The humidity sensitivity increased with the surface roughness (porosity) of the film, and has been further increased when the Ag NPs were used. The SAW sensors with chemically deposited highly porous Ag films have a maximum sensitivity of 80 kHz/65\%RH. The SAW sensors with Ag NPs have the highest sensitivity up to 800 kHz/75\%RH. The SAW sensors with Ag particles showed a strong non-linearity, and explained by the different chemisorption capabilities of the Ag and LiNbO\textsubscript{3} surfaces.

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