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APPLICATION OF SILICALITE-1 FILM TO A SURFACE ACOUSTIC WAVE DEVICE SENSOR

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Abstract – Preparation of silicalite film on a single crystal quartz and its application as a SAW device were investigated. A layer of silicalite crystals was synthesized on a delay line in an interdigital transducer having a dual delay line configuration through the vapor phase transport method. To study the sensitivity and selectivity as a chemical sensor, the SAW sensor was tested in N_2 flow containing vapors of water, acetone, and benzene, respectively. In this study, the sensitivities of the silicalite-coated delay line became tripled for moisture, doubled for acetone, and increased for benzene, compared to that of the bare delay line.

Key words : SAW Device, Silicalite Film, Vapor Phase Transport Method

INTRODUCTION

General requirements for gas sensors are high sensitivity, short response time, reversibility, and high selectivity. In addition, small size, light weight, long operational life and low cost are desirable. Surface acoustic wave (SAW) devices appear to be very interesting because of their low detection limits for the molecules adsorbed, and their relative simplicity [Nieuwenhuizen and Harteveld, 1994]. For SAW devices, sensitivity and selectivity can be achieved by coating them with substances that interact physically or chemically with the molecules of interest [Amati et al., 1992]. Since the response is non-selective, a number of organic and organometallic coatings on SAW devices have previously been explored to impart chemical selectivity [Reinbold et al., 1994; Yuquan et al., 1994]. For this purpose, Battenberg et al. [1996] synthesized and tested organometallic complexes as sensitive layers on quartz microbalance devices. They found that sensitivity and selectivity depend critically on the metal contained in the organometallic materials. Chang et al. [1991] deposited and tested different phospholipids and fatty acids on the surface of the SAW devices with Langmuir-Blodgett technique.

In general, if a chemical reaction occurs between the gas and the interface material, good selectivity is obtained, but partial or totally irreversible responses are observed. If molecules undergo physisorption, interaction between the gas and the interfacial material is weak, and the response is reversible, but low selectivity is obtained. From these considerations, it can be deduced that the use of SAW sensor as efficient analytical tool is strongly limited by the lack of selectivity or reversibility of their responses [Liron et al., 1993].

A method for solving the problem of poor selectivity may be the use of an array of sensors in conjunction with pattern-recognition software [Sonov et al., 1996; Ping and Jun, 1996]. The identification of odor, depending on the species of lipid used for coating, can be expressed in terms of the similarity of the normalized resonance frequency shift pattern. It is possible to vary the selectivity of the system by using plural sensors with different sorption membranes. In this regard, zeolite coatings could increase the number of arrays of sensors due to their diverse sorption capacities and selective properties depending on their diverse pore sizes and compositions. To overcome the irreversibility of the selective sensor coatings, the active surface can be heated to remove the species chemically adsorbed.

Inorganic films have high thermal stability and high chemical resistance. Sun et al. [1993] synthesized porous silica coatings on a quartz crystal by the sol-gel process and tested it as a humidity sensor. The resonant frequency of the coated quartz resonator decreases with increasing relative humidity. Bein et al. [1989] explored a strategy of introducing the molecular sieving function of zeolites into SAW sensors because the zeolite films offer high thermal stability, surface area and chemical resistance. They deposited the zeolite/silicate suspensions by dip-coating. When the solvent was evaporated, zeolite crystals were consolidated on the support by viscous sintering. Koegler et al. [1994] grew an oriented coating of silicalite-1 on a silicon wafer to study the nucleation and growth mechanism. To measure concentration of CO_2 in gases, silicalite-1 was applied to a SAW sensor through the post-synthesis dried suspension technique. Plog et al. [1995] used zeolite Y as a gas-sensitive layer material on thin-film interdigital capacitor. A screen printing method of zeolite powder suspension was used as a coating technique. Alberti and Fetting [1994] also used zeolite X in the construction of a selective sensor system for measuring hydrocarbon. A thin zeolite layer was made by spraying an aqueous zeolite suspension. The sensitivity of a gas sensor can be reinforced especially by introducing zeolite coating due to its large internal surface area. Moreover, selectivity can be

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endowed by means of the unique pore size and structure of the zeolite.

In this work, a silicalite crystal film was directly synthesized on the designed area of a single crystal of quartz by the masking method. Interdigital transducers having a dual delay-line configuration were designed and prepared by the photo masking method. The one delay-line (sample line) had a silicalite crystal coating on the sensing area, while the other delay-line (reference line) was left bare. Experimental responses of the silicalite-coated SAW device to the vapors of water, acetone and benzene were measured.

EXPERIMENTAL

A single crystal of quartz (with 2.54 cm diameter and 1 mm thickness) was used as a piezoelectric material for a surface acoustic wave device. Tetrapropylammoniumhydroxide (TPAOH, 40 wt% Johnson Matthey Electronics) and Ludox™ AS-40 were used as starting materials for the synthesis of the silicalite layer on the single crystal of quartz plate in order to produce a silicalite film on the specific area of the quartz surface; an organic polymer material (AC-828, Adcoat CO.) stable at the synthesis condition was employed as a masking substance. Starting materials for the synthesis of the silicalite layer were added to the designed quartz surface in a sequence as follows: one drop of aqueous TPAOH solution was put on the quartz surface, and subsequently one or two drops of aqueous silica solution (Ludox™ AS-40) were added into the TPAOH solution on the quartz. The aqueous TPAOH is immiscible with Ludox. This starting mixture was placed into the Teflon™ cup on top of the quartz crystal shown in Fig. 1. Distilled water (7 g) was also introduced to the bottom of the Teflon vessel. The volume of the pressure vessel was 40 ml. A Teflon bar was used to support a sample holder and to separate the starting materials from the water phase at the bottom. A stainless steel bomb containing the Teflon vessels was sealed and kept in an air heated oven at 423 K for 4 days. Water was supplied to the synthesis gel by the vapor pressure of water under hydrothermal conditions. After synthesis, the bombs were cooled down in air. The resulting silicalite layers on the quartz plates were washed with distilled water and calcined at 823 K for 5 hours. The silicalite layers were investigated by XRD analysis, infrared spectroscopy (IR) and scanning electron microscopy (SEM).

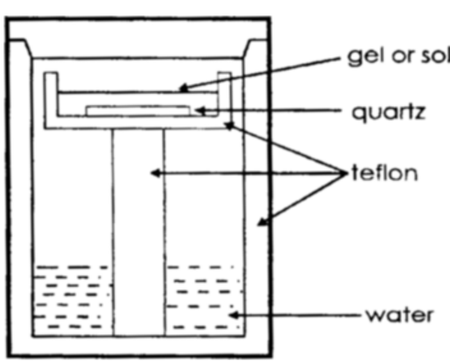

Fig. 1. Experimental arrangement for silicalite film synthesis.

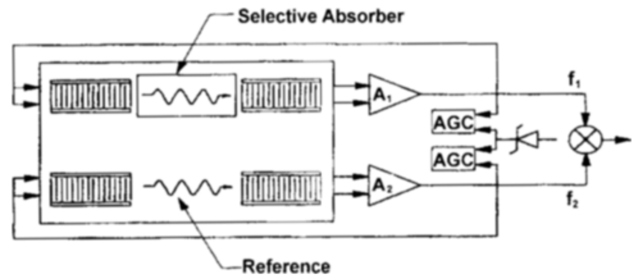

Fig. 2. Dual delay-time configuration in the SAW device.

Interdigital transducers having a dual delay-line configuration were designed and prepared on the front and the rear of the silicalite film. The one delay line (sample line) was prepared at the front and the rear of the silicalite coated area (5 mm $\times$ 5 mm) by the photo masking method. The interval and the width of the resonator were 10 μm, respectively. The resonance frequency of the sample line was 84.1085 MHz. The second delay line (reference line) was not coated with silicalite and was used as a reference (its resonance frequency was 84.2210 MHz) as shown in Fig. 2. The interdigital transducers and integrated circuits were installed in a small case that had an inlet and an outlet path for gas flows.

A measurement system of the SAW sensor was composed of gas flow lines and an evaporator, interdigital transducers and sensing areas (the areas between the interdigital transducers of the delay lines), electronic measuring circuits and a frequency counter. All of the flow lines were constructed from 1/8 inch stainless tubes and 3-way valves.

The pure (99.99 %) N_2 gas was purged over the measuring surface of the sensor for an hour in order to clean the measuring surface. To prepare sample gases, N_2 gas passed through water or organic solvents (acetone and benzene) maintained at constant temperature. The exit gas was introduced to the sensing areas by manipulating a three-way valve for the measurement test. The carrier gas N_2 flow rate was 60 cm^3/min. All lines were heated externally to 318 K to prevent condensation on the inner surfaces of the lines. The SAW sensor was installed in an oven maintained at 308 K. The frequency variations of the each delay line following the gas adsorptions on the sensing area were recorded. The gas stream was switched from the pure N_2 gas to the vapor containing gas.

RESULTS AND DISCUSSION

Liquid sols or mixtures having specific compositions can be transformed into zeolites at 423 K [Kim et al., 1993, 1995]. In comparison with the conventional hydrothermal synthesis method, the vapor phase transport method can cut down the amount of chemicals and waste disposal problems. However, the reproducibility of the silicalite film syntheses was lower than that of the powdered zeolite syntheses, because of the heterogeneity of the starting materials.

Silicalite film coating was formed on the designed area (5 mm $\times$ 5 mm) of the quartz surface by using the masking substance as shown in Fig. 3. Silicalite crystals were formed sparsely onto surface as shown in Fig. 4. Most of the silicalite crys-

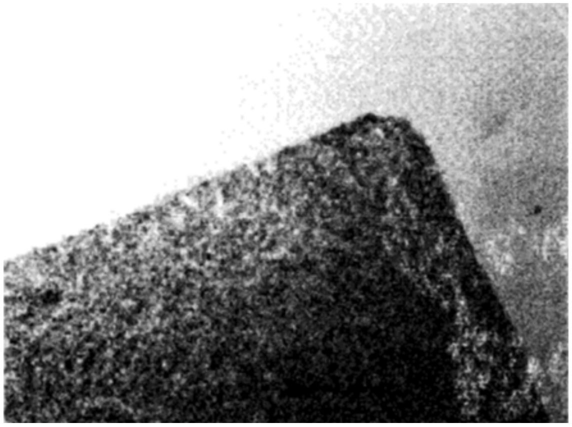

Fig. 3. Silicalites grown on a designed area (5 mm×5 mm) of a quartz plate.

tals on the surface have a specific orientation. The straight channels of the silicalite perpendicularly meet with the quartz surface [Iwasaki et al., 1996]. This result illustrates that the number of nucleation sites was restricted by the clean polished surface, and the crystal growth started from the surface. In water vapor stream (the saturated vapor pressure was 14.5 mmHg), the frequency decrease of the uncoated delay-line was 500 Hz due to surface loading of the moisture. By comparison, the frequency decrease of the silicalite-coated delay-line was 1540 Hz. Although the measuring areas were the same, the sensitivity of the silicalite uncoated surface area was three times as high as that of the uncoated surface. When dry N_2 was passed again over the saturated measuring surfaces, the resonant frequency of the uncoated delay-line went back to its initial frequency. However, the frequency of the silicalite-coated delay-line did not return to its original frequency and was still 160 Hz lower than its initial frequency due to the residue molecules adsorbed in the silicate layer at 308 K. When the saturated N_2 was passed over the previous sensing areas a second time, the frequency variations were

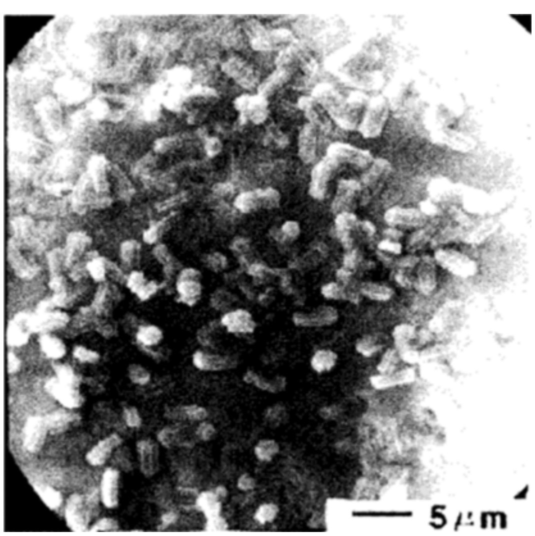

Fig. 4. Silicalites grown on a clearly polished quartz surface.

similar to the values previously obtained (i.e., 500 Hz from uncoated delay-line and 1,540 Hz from the coated delay-line were obtained, respectively).

After the measuring surface was cleaned with dry N_2, N_2 containing benzene was tried using a three-way valve. A decrease of 900 Hz was measured from the uncoated delay-line using the stream of N_2 containing benzene. By comparison, a decrease of 1,400 Hz was obtained from the silicalite-coated delay-line. The sensitivity of the silicalite-coated surface was higher than that of the uncoated surface. The frequency decreases with the increasing vapor pressure of liquid benzene, as shown in Table 1. When dry N_2 was utilized again over the saturated measuring surfaces, the frequencies of the delay-lines did not return to their original frequencies within 5 minutes. Moreover, they were still 40 Hz lower in the uncoated line and 450 Hz lower in the coated line than the initial frequencies. However, the frequencies of the delay-lines approached the original frequencies under dry N_2 flow conditions for 2 hours.

The decreases in frequency were also measured when using N_2 containing acetone. The frequency decreases with increasing temperature of liquid acetone as shown in Table 2. The silicalite-coated delay-line had twice the sensitivity. The silicalite-coated surface shows a high selectivity for acetone. When dry N_2 was utilized again over the saturated measuring surfaces, the frequencies of the delay-lines did not return to their original frequencies within 5 minutes. Moreover, they were still 700 Hz lower in the uncoated line and 2,360 Hz lower in the coated line than the initial frequencies. It can be mentioned that sensor irreversibility is increased with its sensitivity. The frequencies of the delay-lines approached the original frequencies under dry N_2 flow for 5 hours.

It is confirmed that SAW device sensitivity can be increased by silicalite coating. It is expected that the potential for practical use of SAW sensors will be increased, once diverse compositions and structures of zeolites are fully utilized. Irreversible adsorption on SAW sensors can be solved by attaching a heating element on the backside of the sensing area. Applications of the zeolite layer on SAW sensors need more work, but they will broaden the possibility for the practical use.

Table 1. Frequency changes according to the vapor pressure of benzene

Temp. of benzene (K)	△F in uncoated line (A) (Hz)	△F in coated line (B) (Hz)	B-A (Hz)
293	900	1400	500
303	2600	3280	680
313	2860	3670	810
323	3170	4080	910

Table 2. Frequency changes according to the vapor pressure of acetone

Temp. of acetone (K)	△F in uncoated line (A) (Hz)	△F in coated line (B) (Hz)	B-A (Hz)
293	3150	5720	2570
303	4640	9580	4940
316	5310	14030	8720

CONCLUSIONS

Silicalite crystals were sparsely formed onto the quartz surface; the straight channels in the silicalite meet with the quartz surface perpendicularly. This result illustrates that the number of nuclei was restricted by the clean polished surface, and the crystal growth started from the nuclei at the surface; thus, the crystal growth at the surfaces had a direction.

The frequency decrease in the SAW devices was proportional to the concentration of the vapor. The sensitivities of the silicalite-coated delayed line were much higher than that of the uncoated delay-line. Application of zeolite film to SAW device coating will raise the performance of the SAW sensor and will broaden the possibility for the practical use.

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