Surface acoustic wave interaction with humidity-sensitive $TPPS_4$ nano-strip structure

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Abstract

The surface acoustic wave propagation in the structure consisting of *Meso*-tetra (4-sulfonatophenyl) porphine ($TPPS_4$) film deposited on a piezoelectric lithium niobate substrate has been studied. The SAW velocity decrease and the attenuation increase with growing ambient humidity. This effect is attributed to the changes in the film viscoelasticity due to the water adsorption. Much weaker response is observed when the water vapour is replaced by the acetone vapour. The possibility of using $TPPS_4$ - $LiNbO_3$ structure as a SAW humidity sensor has been demonstrated.

Keywords: surface acoustic wave, porphyne nano-strip structure, humidity sensor

Self-assembled molecular aggregates have attracted much interest because of their tremendous potential for implementation of bioorganic devices. Meso-tetra (4 sulfonatophenyl) porphyne ($TPPS_4$), a water-soluble dye of well defined chemical structure, forms J-type aggregates under appropriate conditions self-assemble into nanometer sized soft cylindrical structures that appear flattened on the substrate surface [1]. It is a promising material for building functional structures on solid-state surfaces [1-3]. From a fundamental point of view, these nanostructures are interesting because they exhibit unusual properties, often quite different from those of single molecules or the bulk material. The electronic coupling in these aggregates makes them potentially useful for application as nanowires, nanometer sized photoconductors or as antennae in synthetic light-harvesting complexes. Surface acoustic waves (SAWs) might open new possibilities for studies and applications of nanostructure complexes. In particular, implementation of various types of physical and chemical sensors is of a great practical importance. Use of surface acoustic waves for sensing applications is based on the sensitivity of wave propagation to surface perturbations. A possibility of using a porphyrin family material, *meso*-tetraphenylporphyrin, in the surface acoustic wave [4] and bulk acoustic wave [5] sensor has been demonstrated, but, as far as we know, no data on SAW interaction with $TPPS_4$ nanostructures is available. The SAW interaction with carbon nanotubes has been studied previously [6]. In this paper, we report on the humidity sensitive SAW propagation in the $TPPS_4$ strip-like nanostructure.

Samples were prepared by spontaneous adsorption of $TPPS_4$ J-aggregates between two interdigital transducers (IDTs) on top of a piezoelectric $LiNbO_3$ substrate as shown in Fig. 1. *Meso*-tetra (4-sulfonatophenyl) porphine ($TPPS_4$) (Frontier Scientific, Inc.) was used without further purification. The solution was prepared by dissolving $TPPS_4$ in a drop of distilled water and then diluted it with hydrochloric acid (HCl) till the required concentration. Films of $TPPS_4$ nanostructures were deposited by casting a drop (20 μl) of the $TPPS_4$ aggregate solution (c= $3*10^{-4}$ mol/l) between the IDTs of the SAW delay line and evaporating it at a room temperature. Drop of the solution covered approximately 6 mm^2 of the crystal surface with the layer thickness of approximately 0,3 μm. The AFM image of the structure shown in Fig. 2 reveals the presence of the strip-like J-aggregate structures. The size of the strips was in the range 4x50x(200-1000) nm. The IDTs for SAW excitation and detection were fabricated by a standard photolithography technique. The spacing between transducers was 15 - 20 mm, and the transducer center frequencies were in the range of 100 -160 MHz.

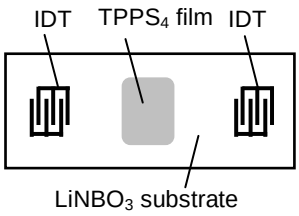

Fig. 1 **Schematics of the structure studied**

We have studied the influence of ambient humidity on SAW propagation characteristics in these structures. For this purpose, the sample was placed into the limited-volume cavity, which was closed immediately after a small piece of wet paper had been put onto its bottom. Typically, the piece of paper had an area of 5x5 mm^2 and contained a few micro-litres of water. The cavity volume was about $100cm^3$.

The changes in the SAW attenuation and velocity were measured as functions of time. The attenuation change was determined from the variation of the radio frequency (RF) pulse (typically of 1 μs duration) transmission through the SAW delay line. The velocity was determined from the frequency variation of the SAW delay-line oscillator consisting of the sample

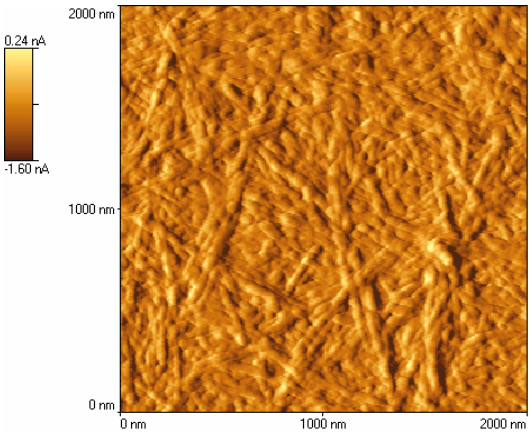

Fig. 2. **AFM image of $TPPS_4$ film**

under investigation connected into the feedback loop of a wideband RF amplifier. The correspondent dependencies are shown in Figures 3 and 4. After closing the cavity, a considerable increase in the SAW attenuation (up to 13 dB) and a noticeable decrease in the SAW velocity (up to 0.12 %) are observed. We attribute these effects to the increase in air humidity in the closed volume due to water evaporation from the wet paper. When the cavity is opened and the wet paper is removed, both the velocity and attenuation exhibit a fast jump towards the initial values, since the excess vapour is distributed in the adjacent space. Our experiment shows that the $TPPS_4$ nanostructures-$LiNbO_3$ substrate system exhibits a fast and pronounced response to the ambient humidity and can be used for sensing purposes.

In a similar way, we have studied the response of the structure to acetone vapour. The relevant curve given in Fig. 4 reveals much weaker response in this case, even at acetone vapour concentrations several times exceeding those of the water vapour. This demonstrates the chemical selectivity of the SAW sensor.

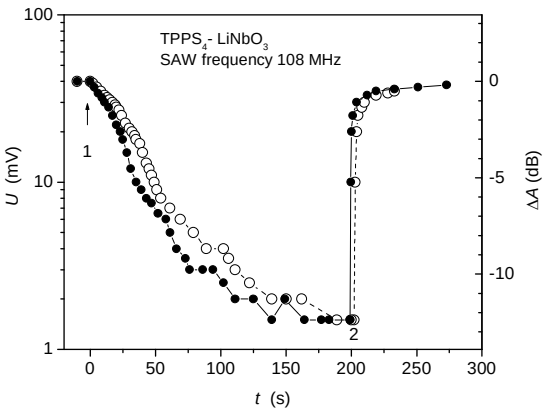

Fig.3. **SAW pulse amplitude *U* at the output transducer and the correspondent change in SAW attenuation Δ*A* as a function of time: (1) piece of wet paper inserted and the cavity closed; (2) cavity opened and paper removed. Two consequent experiments with the time interval of 300 s are represented by full and open circles.**

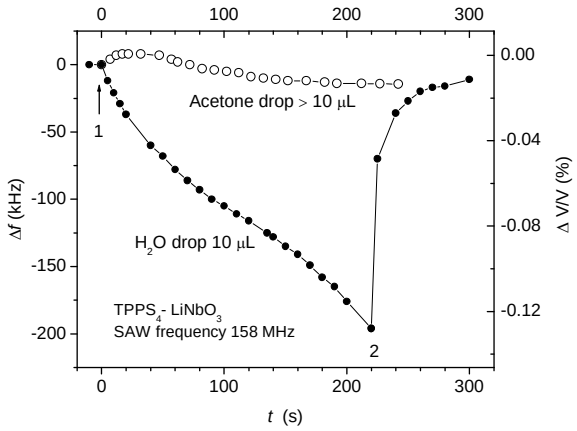

Fig. 4**. SAW oscillator frequency change Δ*f* and the correspondent relative change Δ*V*/*V* in SAW velocity as a function of time: (1) piece of wet paper inserted and the cavity closed; (2) cavity opened and paper removed. Open circles show the oscillator response to acetone vapour.**

Three physical mechanisms - the mass loading, the acoustoelectric interactionand the viscoelastic effect - are known to be responsible for externally-induced changes in SAW parameters [7]. The mass loading leads only to the change in the SAW velocity, whereas the other two mechanisms affect both the velocity and attenuation. We attribute the humidity dependence of SAW parameters in our structure to the change in viscoelastic properties of $TPPS_4$ film. Quantitative estimations of these properties are beyond the scope of this short note.

The qualitative explanation for system sensitivity is as follows. It was reported [8] that the dimensions of formed $TPPS_4$ long stripe-like aggregates, measured by atomic force microscopy, varied depending on the type of substrate. Long stripe-like aggregates were flattened on the substrate surface, and the height and width of aggregates highly correlated with the polarity of SAM surface groups. For example, the J-aggregates were narrower on hydrophobic substrates (with non-polar groups) and wider on hydrophilic substrates (with polar groups). Hence, the presence of water molecules affects the dimensions of stripe-like $TPPS_4$ aggregates, thus changing the viscoelastic properties of the film.

Acknowledgements

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Paviršinių akustinių bangų sąveika su drėgmei jautriais $TPPS_4$ nano juostelių dariniais

Reziumė

Tiriamas paviršinių akustinių bangų sklidimas struktūroje, sudarytoje iš *meso*-tetra-(4-sulfonatofenil)-porfino (TPPS4) sluoksnio ant pjezoelektrinio ličio niobato padėklo. PAB greitis mažėja, o slopinimas didėja, kai aplinkos drėgmės daugėja. Šį reiškinį aiškiname sluoksnio viskoelastinių savybių kitimu adsorbuojant vandens molekules. Pakeitus vandenį acetonu, atsakas būna daug silpnesnis. Parodyta $TPPS_4$-$LiNbO_3$ darinio kaip drėgmės jutiklio panaudojimo galimybė.

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