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THE PHOTOELECTROCHEMICAL ETCHING AS A TOOL FOR GaN GAS SENSOR FABRICATION

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Introduction

The fast industry development in the last decades led to a disaster in ecology by uncontrolled exhaust from manufactories and automobiles, which can be redressed by controling the concentration of pollution gases. Over the last years there have been many reports concerning solid state gas sensors based on SnO_2 [1] for oxidizing gases, Ti_2O_3 [2] for reducing gases, porous silicon for gas sensing of organic vapor [3], as well selective Ga_2O_3 methane gas sensor [4].

One of the highest pollution branch of economy is the transport which use oxygen sensor for monitoring the exhaust. The so called *lambda sensor* based on yttrium stabilized zirconia [5] which operate at elevated temperature (700 K) measures the concentration of oxygen in the exhaust gas in order to keep the air-fuel ratio within tight limits, close to the optimum catalyst efficiency. The malfunction of this sensor lead to exaggerate fuel consume and as result increase of exhaust gas.

In spite of proposed commercial gas sensor, the market still have a stringent necessity in high temperature gas sensors which is easy to use and stable in harsh environment. The best choice could be solid state gas sensor based on GaN with modified morphology.

Experiment

The initial material for sensor is GaN epilayer grown by low-pressure metal organic chemical vapor deposition (MOCVD) on sapphire using trimethylgallium and ammonia as source materials. A buffer layer of about 25-nm thick GaN was first grown at 510°C, while the top n-GaN layer with 1.3–2.0 μm thickness was grown at 1100°C. The concentration of free electrons in the top n-GaN layer was $1.7 \cdot 10^{17} cm^{-3}$.

To achieve good ohmical contacts, Ti/Au metals deposited by e-beam evaporation were used. Thermal annealing at 600°C in argon environment during 5 minutes was performed for hardening the material and increasing of metals adhesion to GaN surface. After cleaning in buffered HF solution for carbon removal and 30% HCl for oxide removal, the sample was fixed in etching cell using Ag pasta.

The photoelectrochemical etching was performed in 0.5 M KOH under 200 W Hg exposure during 10 minutes at room temperature. If the solution is untouched, columnar structure is obtained (fig.1,*a*), and whisker morphology is obtained in case the solution is agitated (fig.1,*b*).

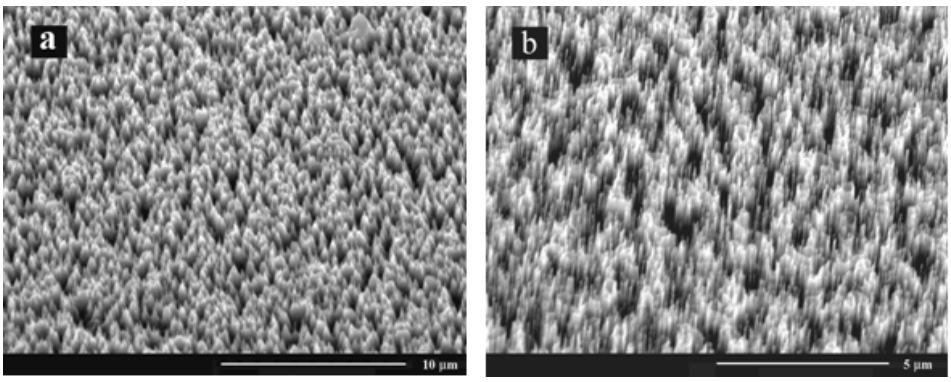

Fig.1. SEM images taken from etched samples in untouched solution (a) and agitated (b)

Results

To evidence the gas response of the obtained structures to ethylic alcohol vapor and hydrogen, the

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samples were heated in the range of 250 to 360°C in a special gas cell which allows to control the gas flow, temperature and resistivity acquisition in time, as depicted in fig. 2 and 3.

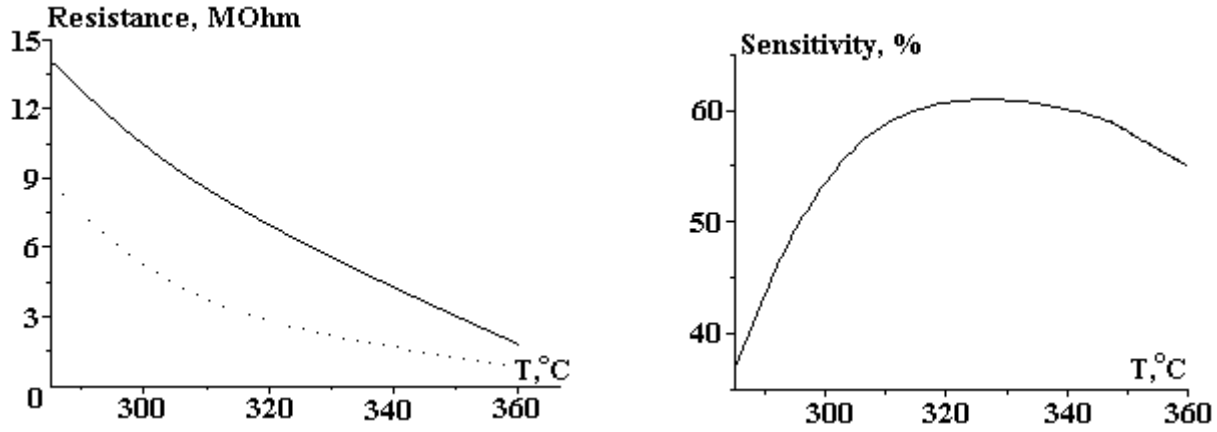

Fig. 2. Dependence of resistance in dry air (solid line) and 0.05% C_2H_5OH vapor (dot line) upon temperature (left), and sensitivity versus temperature for the same concentration of ethylic alcohol (right)

The sensitivity was calculated using formula:

$$S = \left(1 - \frac{R_{gas}}{R_{air}}\right) \cdot 100\%,$$

where R_{gas} is the resistance in gas medium and R_{air} – resistance in dry air.

Experimentally it was determined that better sensitivity to volatile vapors such as ethylic alcohol is exhibited by whisker like morphology (fig.1,*b*) whereas for hydrogen detection columnar structures (fig.1,*a*) is more suitable. I succeeded to detect ethylic alcohol down to 0.01%.

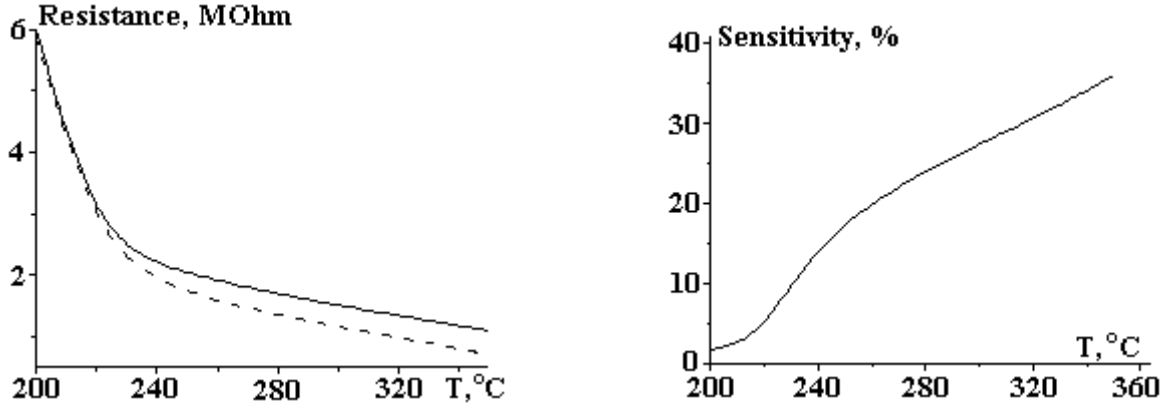

Fig. 3. Dependence of resistance in dry air (solid line) and 0.1% of H_2 (dot line) upon temperature (left), and sensitivity versus temperature for the same concentration of hydrogen (right)

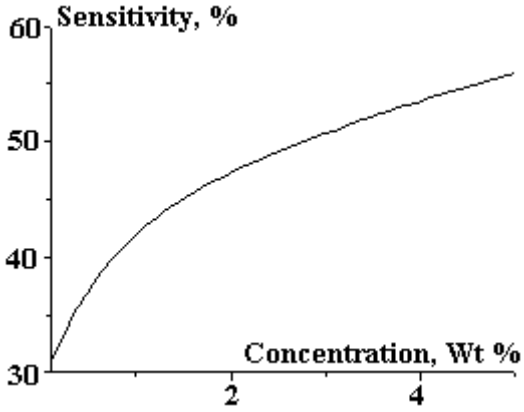

Fig.4. The sensitivity dependence upon concentration of hydrogen in weight % at 325℃

In fig. 4 is presented the dependence of sensitivity versus hydrogen concentration, indicating that there is no saturation in this range.

The mechanism for volatile compounds sensitivity was discussed in literature [6, 7]. It is supposed that on heated surface alcohol dissociates in hydrocarbon radicals which changes the carrier concentration at the surface of semiconductor. As a result, changes in resistance can be registered. In case of hydrogen, molecular dissociation on semiconductor surface occurs, the process being amplified with the temperature. Figure 3 shows the nearly linear dependence of the sensitivity as a function of temperature, which is in good correlation with the theory.

The response time measured at the range 0.1 to 0.9 from maximum value did not exceed 10 s, but the recovery time was in the range from 5 minutes for hydrogen to 20 minutes for alcohol vapors at 325°C. The high value of the response time for alcohol is the result of dissociated radicals trapped at the semiconductor surface, which can be improved using exposure to oxidized gas (ozone for instance) after each alcohol detection, or shot thermal shock, at temperatures higher than 500°C.

A design for commercial application in alcohol detection is proposed. The Pt heater is deposited on sapphire side using e-beam evaporation and standard lithography. On top GaN Ti/Au ohmic contacts were deposited and photoelectrochemical etching process was performed. The prototype is presented in fig.5.

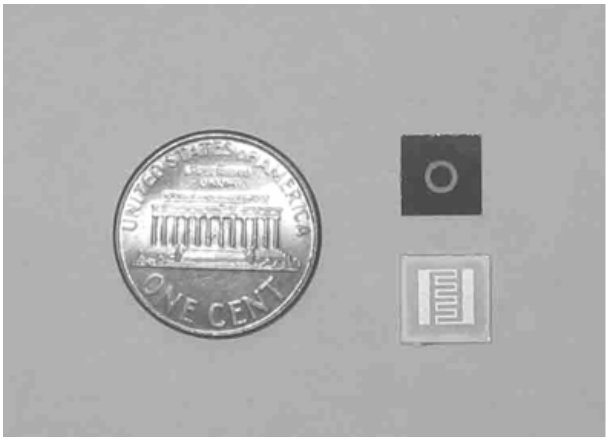

Fig. 5. The prototype of GaN gas sensor for alcohol detection with Pt heater on sapphire side presented on the right-down corner

4. Conclusion

We demonstrated the perspective of photoelectrochemical etching of GaN as a technological tool for solid state gas sensor fabrication.

The sensor did not show memory effect and was stable during prolonged exposure to gases. Due to high temperature operation there is an effect of self cleaning of the surface and minimum influence of air humidity.

Good sensitivity and short time response make this type of sensors suitable for commercialization.

Acknowledgements

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Summary

Whisker and columnar structures of GaN were fabricated using photoelectrochemical etching in KOH solution. The conductivity changes of the obtained structures to ethylic alcohol and hydrogen were studied. Optimized design for sensor fabrication is proposed.