

CHALCOGENIDE SEMICONDUCTORS AS GAS SENSORS

Tsiulyanu Dumitru

Technical University, Department of Physics, bul. Dacia 41, MD-2060, Chisinau, Moldova

Abstract: A brief survey of experimental results to gas sensing with chalcogenide semiconductor based devices is given. It is pointed out that physical phenomena such as electrical conductivity can be coupled to chemical reactions on the surface or within the sensing material. Sensors based on tellurium alloys for detection of nitrogen dioxide, ammonia or carbon oxide are described in some detail. A general discussion is given about the fundamental mechanisms of gas sensing with these materials taking into consideration their special chemistry and defect states.

Keywords: Gas sensors; Chalcogenide semiconductors

1. INTRODUCTION

The possibilities of detection of contaminating gases in the atmosphere by means of semiconductors are being investigated intensively since middle of the last century, when Brattain and Bardeen discovered [1] the effect of gas adsorption on germanium conductance. This topic has both scientific and technical importance caused by global environmental pollution. Basic scientific principles of direct gas sensing consist in variation of one of the properties of the species itself like thermal or electrical conductivity, sound propagation, optical absorption, reflection or fluorescence. Conductive gas sensors are most attractive because they are compact, sensitive, have low cost, and have low power consumption.

In this article conductive chalcogenide semiconductor gas sensors operating at room temperature are primarily discussed. This is a novel class of gas sensors recently proposed for monitoring pollutants in ambient air [2 -3].

2. EXPERIMENTAL

Chalcogenide semiconductors are called solid-state materials, which comprise chalcogen elements from the sixth group of the periodic table S, Se or Te. The peculiarities of chalcogenide materials are due to unique electronic structure of chalcogen's atoms, which comprises lone - pair electrons. These electrons can be excited or even become free without breaking some valence chemical bonds.

The chalcogenide alloys are usually prepared from pure elements by the melt-quenching method. The melting temperature and the synthesis time depend on composition and vary from 200 to 1000⁰ C and from 10 to 100 h respectively. Gas sensitive thin films usually are prepared by

vacuum thermal evaporation of synthesized materials onto Pyrex glass, ceramic or silicon substrates.

The morphology of the films depends on the deposition rate and substrate temperature. Usually the films are polycrystalline with grain sizes of about 0.5 to 1.0 μm , which are orientated along the substrate or without preferred orientation.

3. RESULTS AND DISCUSSION

Figure 1 shows the typical current flow through a sensor based on tellurium alloys under repeated switching on-off of the NO_2 gas mixture at constant bias voltage. Squared pulses of NO_2 vapor with concentration of 0 ppm, 0.75 ppm, and 1.5 ppm were applied. The dotted line shows the switching schedule. It is seen that the current follows the schedule and the recovery time is longer than the response time. It is significant that there is no baseline drift or noticeable drift of the gas induced current.

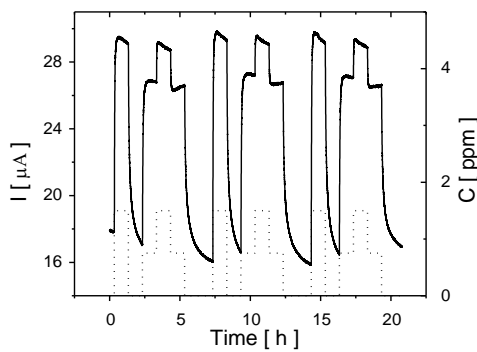


Fig.1. Transient characteristics of gas - induced current by exposure to NO_2 according to the profile shown in dotted lines of the bottom.

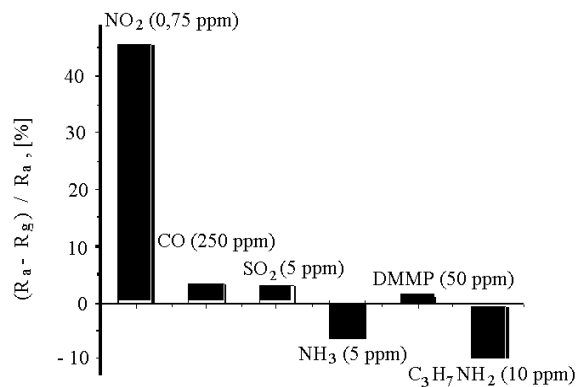


Fig.2. The sensor response to various gases

Figure 2 illustrates the response of the sensitive films to various test-gases at operating room temperature. The sensor exhibits a high response towards small concentrations of NO_2 but the cross-sensitivity to other gases such as CO , NH_3 , SO_2 , $\text{C}_3\text{H}_7\text{NH}_2$ and DMMP is low. The most tested gases exhibit the increase of sensor conductivity but propylamine and ammonia show a vice-versa influence.

The mechanism of gas detection by chalcogenide semiconductors is still not completely understood, but the reason of gas sensing with these materials seems to be the lone-pair electrons, which form the upper part of the valence band. If the crystalline network contains defects such as unsaturated chemical bonds (dangling bonds) the interaction between these defects and lone - pair

electrons occurs. The dangling bond interacts with neighboring lone - pair, bonding with it by distorting its environment [4]. Such interaction results in formation of lattice defects and release of about $10^{13} - 10^{15}$ holes / cm^3 , which causes the p- type of conductivity. The lattice defects create the rather deep acceptors situated below the center of the gap i.e. closely to top of the valence band.

Figure 3 shows the possible model of dangling bonds - lone pair electrons interaction and the surface state bands at the chalcogenide semiconductor's surface. It is seen that the hole enriched (an accumulation) region is formed at the surface, grain boundary and intragrain regions.

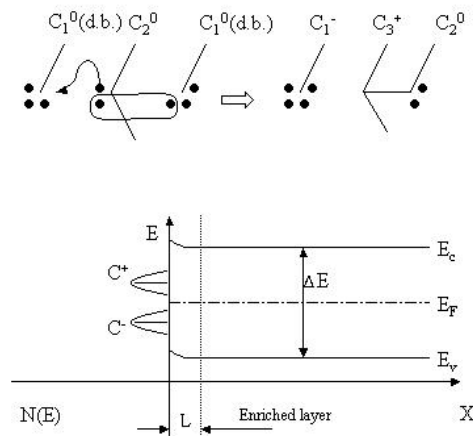


Fig.3. The model of the dangling bonds - lone pair electrons interaction and the surface state bands at the chalcogenide semiconductor's surface.

When the chalcogenide semiconductor is introduced into gaseous environment the adsorption of gas molecules occurs, which can produce either - donor or acceptor levels. Let us for example consider the adsorption of nitrogen dioxide. The molecule of nitrogen dioxide has an odd electron [5] that is after covalently bonding of nitrogen to oxygen one of the atoms remains with a single unpaired electron. Being adsorbed on the surface of the chalcogenide semiconductor the molecule of NO_2 act as a dangling bond, that can accept a lone - pair electron to form an electron pair. Capture of a lone - pair electron means the transition of an electron from the upper part of the valence band to a NO_2 acceptor level, which result in realize of an additional hole. Thus, the adsorption of nitrogen dioxide leads to increase in the majority carrier density in the grain boundary and intragrain region, which results in increasing of the film conductivity. Obviously, chemisorbtion of others gases implies others surface reactions that can lead both to increase ore decrease the majority carrier density in the grain boundary region and hence to increase or decrease the conductivity of the film.

In fact the response of tellurium based films to ammonia was shown [6] to arise from reduction of tellurium oxide atoms present on the surface and intergrain regions, which also act as

acceptors. Thus, to develop a selective sensor for the definite gas the chalcogenite material with definite composition has to be chosen.

CONCLUSIONS

Due to special chemistry and structure, chalcogenides materials can be used in development of effective gas sensitive devices. The flexible structure and large ability for alloying allow enormous properties variation of these materials and give the possibility to design the selective sensors to different gases. The sensors can operate at room temperature and show considerably short response times as well as sensitivity in the ppm and sub-ppm concentration range.

REFERENCES

- [1] W.H. Brattain and J. Bardeen, Bell Syst. Techn. J., **32** , (1953) 1-15.
- [2] S. Marian, K. Potje –Kamloth, D. Tsiulyanu, H - D. Liess, Thin Solid Films, 359 (2000) 108-112.
- [3] D. Tsiulyanu, S. Marian, H - D. Liess, Sens. Actuators B 85 (2002) 232-238.
- [4] M. Kastner and H. Fritzsche, Philos. Mag. **B 37**, (1978),199 – 215.
- [5] . J.Greyson, *Carbon, Nitrogen and Sulfur pollutants and their determination in Air and Water*, Marcel Dekker Inc., New York (1990)
- [6] S. Sen, K.P. Muthe, N. Joshi, S. C. Gadkari, S.K.Gupta, J. M. Roy, S.K. Deshpande, J.V. Yakmi, Sens. Actuators, **B 98**, (2004) 154-159.