BINARY OXIDES SEMICONDUCTOR TRANSDUCERS FOR H_2S SENSORS

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Abstract

The physical processes of semiconductor and heavy metals oxides sensors on H_2S are investigated and possible physical mechanisms of gas sensitivity in the atmosphere of air and nitrogen are considered. Mechanism of adsorbtive-desorbtive sensitivity of heterostuctures to H_2S is connected with conductivity variation caused by the hydrogen atoms diffusion to the boundaries.

duction

vell known that H_2S is one of the most agressive gases which actively interacts with ent materials' surfaces and one which is to be seriously controled in ecological ns monitoring. The physico-chemical criterion for the material selection in gas rs construction is the minimal chemical compounds formation energy for sulphur ıydrogen atoms. This criterion realization gives possibility to construct sensitive nts with relatively low working temperature. In accordance with the principle, thin ium chalcogenides' and heavy metals oxides' layers have the minimal chemical s formation energy with S and H atoms and thus, they are the most favourable for ensors constructions. Besides the mentioned, the cadmium chalcogenide metalloid he similar chemical nature with sulphur atoms. High sensitivity to H_2S in the nce of SO_2 and O_2 of air is enough important in the practical meaning.

ample manufacturing method and measurements

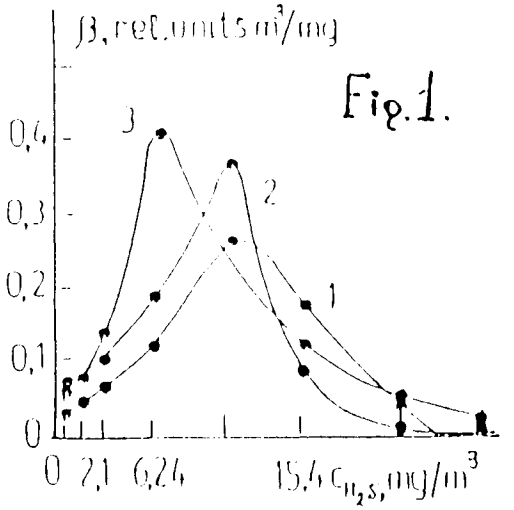
semiconductor films were obtained by the method of thermal evaporation in high m and by the MOC technology. Binary oxide semiconductors were obtained in the ss of sequent coating of sitall substrates by each of the components with previously ited Ohmic contacts. Electronic properties of CdS, CdSe thin films and of Zn, Cd, ı, Pb oxides obtained at different technological conditions were investigated. Gas ive parameters of such structures contacting with H_2S were investigated in the

concentration region of 0-40 mg/m^3. The gas-carrier concentrations in the test camera were varied by the generator GR-645 (USSR) producing specifically pure nitrogen or air. Adsorbtive-desorbtive sensitivity (ADS) was measured according to methods [1].

Results and discussion

Semiconductor CdS, CdSe thin films

CdS, CdSe films' adsorbtive-desorbtive sensitivity to H_2S measured at temperatures (420 -530) K in the pure nitrogen atmosphere was significant and achieved the values of 0.3 relative units/mg.m3 in the gas concentrations region 10-20 mg/m^3.
The degradation processes of ADS were registered for higher temperatures [2]. High sensitivity of CdSe layers was experimentally established for the surface additionally doped by Se atoms and then measured in the presence of H_2S (3-5) mg/m^3 microconcentrations, at temperatures 420 K. Such new conditions were characterized by the transition processes times equal to (1-2) minutes. And the ADS sign changed, for the Se atoms doping level N_{Se}= 10 ^{16} cm $^{-2}$ and the H_2S concentration C_{H_2S}>10 mg/m^3. (Fig.1. curve 1)



Such a behavior of ADS sign, when the surface centres interact with the gas-adsorbate is conditioned by the electroconductivity inversion on the semiconductor surface [1]. The reversable changes of electroconductivity while H_2S adsorbtion on the films surfaces is connected with H_2S surface diffusion difficulties. Especially this phenomena is evident for CdSe:Se films with a high Selen atoms contain. CdSe:Se sensitivity to SO_2 adsorbtion in the H_2S concentration region (1-300) p.pm in the inert medium was practically absent. Evidently, this is connected with SO_2 particles' adsorbtion hinderncе on the surface centres connected with Se atoms, which are chemically similar to SO_2. The fact that S and Se atoms are the adsorbtion centres for H_2S on the semiconductor surface is confirmed by the strong ADS dependence on the atoms' concentration.
Measurements fulfiled at these same temperatuers but in the air atmosphere of high purity show the CdSe, CdS films' sensitivity failure. This fact may be explained by oxygen interaction with surface adsorbsion centres that causes it's passivation. The measurements temperature increase to more than 530 K causes the electroconductivity instability in time.

Heavy metals oxide films

Heavy metals oxides'surfaces interaction with H_2S in the presence of inert highly purified nitrogen medium causes the irreversible initial conductivity changes. The measurements temperature increasing will only enhance the differences between initial conductivity values. When ADS is measured in the atmosphere of air, then the ADS values to H_2S

are comparatively higher and are more than 0.1 relative units/mg m^3, that is achieved in the temparature region 550 K. At the same time, transition processes time τ_b 3-5 min is neccessary for the initial electroconductivity values restoration. Time τ_b was more than 10 min when the temperature was lower. Fig.1 (curves 2-4) presents the results for the most sensitive films ZnO, SnO_2, PbO correspondingly at the temperatures 630 K in the air. In comparison with CdSe:Se films, the ADS maximum for such films is in the region C_{H_2S} =(14 - 30) mg/m^3. Lower ADS values at T=550 K are connected with the lower chemical reactions rate on the semiconductor surface. The H_2S adsorbtion by solid state surface is specified due to H_2S dissociation. Oxide metals interaction with H_2S at T>550 K due to it's dissociation causes chemical reaction with lattice oxygen producing SO_2 and H_2O that reevaporate into the pas phase. In the case of inert medium the surface structure irreversible changes took place, that were registered in the experiments. Measurenments in the atmosphere of oxygen show the initial electroconductivity values restoration, which happens due to surface oxidation after H_2S action. Temperature elevation stimulates the H_2S dissociation rate increase, and thus the oxidation reactions of metal atoms appeared on the oxides surfaces. Proposed mechanism for H_2S interaction with the oxides metal surfaces explains it's donor influence. The ADS increase may also be caused by the film's oxygen defectness level (oxygen vacancies concentration). It is due to the fact that S atoms being on the metal surface tend to fill oxygen vacancies, having chemical properties similar to metalloid. Nevertheless, S-atoms diffusion into the bulk of the layer will not take place because of their ion radius size being comparatively more than of oxygen atoms'. That is why the main S- ions influence is connected with their action on the surface. At the same time, hydrogen atom because of it's high mobility may penetrate into the bulk of the layer thus compensating the bulk's and surface's acceptors, hence changing the intergrain barrier. The oxygen vacancies concentration decrease will brake the S-ions sorbtion and in such a away - the hydrogen ions formation.

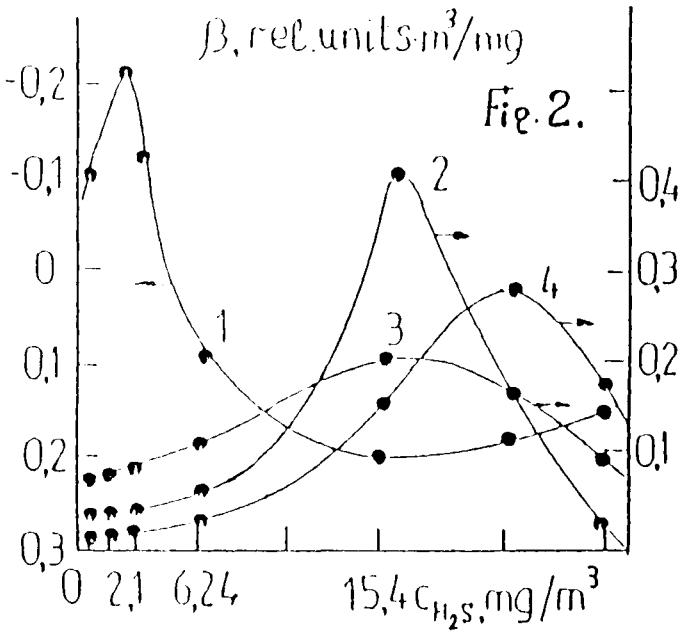
The semiconductor lattice's oxygen evidently plays also the role of S-atoms oxidizer. Development of this oxidation reaction must influence the transition processes times: at adsorbtion -τ_a, at restoration (desorbtion) - τ_r. The registered $\tau = f(C_{H_2S})$ dependence supports such supposition.

The H_2S concentration increase will result in these τ-parameters increasing, The condition $\tau_a > \tau_r$ is always fulfilled for the investigated temperature interval. Heavy metals oxides' films have H_2S sensitivity maximum in the concentration region 14-30 mg/m^3., Fig.1. At the same time ADS shift to the low concentrations regions has place for ZnO films.

Binary oxides films

Achievement of ADS high values to H_2S microconcentrations in the presence of selective sensitivity to SO_2 is an important practical problem which may be solved by consideration of binary oxides' films properties.

Binary oxide structures, obtained by the method of sequent deposition of components had the high values of ADS for H_2S microconcentrations. Fig.2(curves 1,2,3) presents ADS =$f(C_{H_2S})$ dependencies in the presence of pure air for the most sensitive sensors ZnO:SnO_2; ZnO:PbO; SnO_2:PbO, respectively at the temperature 590 K. As it may be seen the ADS maximum is shifted to the lower concentrations region in comparison with it's one component oxides' behavior. This tendency is especially developed for the PbO containing layer. Such



heterostructures showed the di type volt-current dependence, and SnO_2:PbO based structures had most significant rectifica coefficient equal to 65.

So by this means the current f through the sample was controlled the heterostructure barrier potent formed at the contact of t materials. The interoxides bar height is caused by the presence o and S radicals due to H_2S adsorbti The barrier height variation may influenced by the hydrogen ato penetration into the barrier regi This view is supported by the resu of relaxation constants measurements obtained during molecules' adsorbtion/desorbtion processes on the different thickness d- laye Increasing of d corresponds to the increasing of τ-value. The minimal value of τ l place for the thin (0.1 mkm) PbO layers.

This can be explained by the fact that hydrogen has the minimal bonds' formation ener only with Pb atoms. In the case of thinner layers both rectification coefficient and AD decrease. If it is considered that electroconductivity increases according to t exponential law with the barrier potential then ADS will be greater for the grea potential barrier of samples. This conclusion is confirmed by the result that SnO_2 :Pt structures had the most rectification coefficient.

Validity of ADS mechanism is supported by the results of ADS investigation influenc by SO_2 adsorbtion. ADS value for SO_2 at the C_{SO_2} = 28.3 mg/m^3 was 65 times less th for H_2S at C_{H_2S} = 10.3 mg/m^3. These structures had the greater selectiveness to H_2S the presence of SO_2 than the heavymetals oxides.

Conclusion

Thin CdSe films doped by Se atoms have high ADS value for the H microconcentrations and high selectiveness in the presence of SO_2 at the experiment conditions: T = 420 - 530 K and inertia nitrogen medium.

Construction of H_2S sensors operating in the air necessitates employment of binary oxi layers on the base of SnO_2 :PbO. They have maximum selectiveness equal to 65 to H_2S the presence of SO_2 and maximum sensitivity to H_2S when it's concentration is 7 mg/m

References

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