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Mössbauer spectroscopy in determining the gas molecular state

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Abstract A possibility of conversion electron Mössbauer spectroscopy for determining the gas molecular state is shown. For acceleration of gas interaction with active surface the thin iron layer enriched with ^{57}Fe was applied on aluminum foil and gas discharge is used.

Keywords Mossbauer spectroscopy · Mössbauer resonance sensors · Gas analyze

1 Introduction

Determination of the gas molecular state is an important task in the chemical industry and in the manufacture of semiconductor devices, where toxic gases such as phosphine (PH_3), also called hydrogen phosphide, (a colorless, flammable, extremely toxic gas with disagreeable garlic like odor) can be produced. The activation analysis allows only determining the presence of some elements but cannot determine the exact elemental composition which is implied by the molecule formula. Currently, there is a method of gas identification based on resonant absorption of gamma-radiation by the ^{57}Fe nuclei. The method was discussed in [1] as Mössbauer absorption method of analysis (MAMA) of impurities in gaseous media and different types of gamma-resonance (GR) absorbents were considered too. The methods of obtaining such absorbents and their reaction with ammonia are described in [2, 3]. The change of the iron state is produced by substitution of the iron surroundings after absorption of the analyzed molecules. Gamma-ray-absorbents are developed on the basis of neutral porous copolymer of styrene and divinibenen (polysorb) with a pore size of 12-

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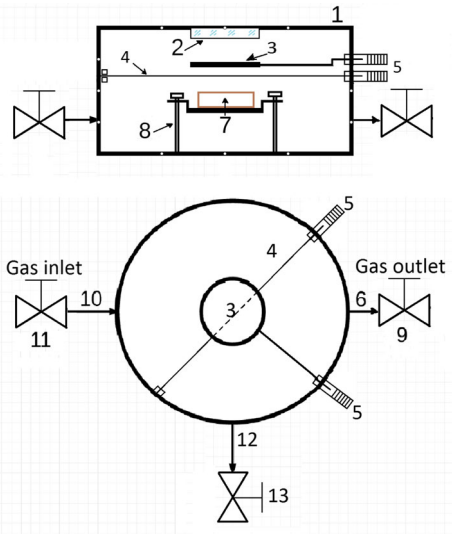

Fig. 1 Schema of experimental device(experimental arrangement): 1) cylinder corpus, 2) window (15 microns aluminum foil), 3) plate anode(0.5 mm beryllium foil),, 4) wire anode, 5) high voltage connector, 6) gas outlet choke, 7) absorbent, 8) absorbent holder, 9) outlet faucet, 10) inlet choke,11) inlet faucet, 12) choke for vacuum pump, 13) faucet for pump

100 nm, impregnated with iron chloride solution. After heating Fe(III) is reduced to Fe(II) ($FeCl_3 \rightarrow FeCl_2$). After ammonia treatment the compound $Fe(OH)_3$was obtained according to the reaction $FeCl_2 \times 4H_2O + NH_3 \rightarrow Fe(OH)_3 + NH_4OH + NH_4Cl$. $Fe(OH)_3$ has known Mossbauer spectra parameters IS=0.41±0.05 mm/s, QS=0.65±0.05 mm/s. The iron atoms are in compounds containing chlorine. In this method the special chemical compositions must be found because the final result of the interaction is the phase $Fe(OH)_3$ for any gas. Besides, this method requires a large amount of gas. The ferric chloride represents paramagnetic compound. The result of interaction of this compound with gas is a paramagnetic phases too. Their spectra lines may coincide. It complicates interpretation of spectra and gas.

Conversion electron Mössbauer spectroscopy(CEMS) was used to study tin-bismuth (Sn-Bi) oxide films prepared by spray-pyrolysis techniques [4]. Tin-bismuth oxide was an CO selective gas sensor. Sn-Bi oxide films were exposed for one day at temperatures 20-500 °C. The state of $Sn^{4+}$was a little affected by the interaction with incoming gases, such as 5% CO+95% He and 5% CH_4+95%He, especially CO gas. A decrease in IS was observed with increasing temperature. There were the differences in spectra but they are not very grate in 2 types of investigations.

This paper in fact is an attempt, which is made for investigation gas molecular state using (CEMS) and iron sensors. The purpose is to prove that not only an impurity compound can be identified, but also the state of this impurity molecule can be investigated. For example, this method may solve the issue of whether or not the state of ionic liquids in the gas phase pairwise. The gases NH_3 (liquid ammonia) and N_2H_4. (hydrazine), which have identical elements but a different chemical state, were chosen for demonstration.

Ammonia (NH_3), colorless, pungent gas composed of nitrogen and hydrogen. It is the simplest stable compound of these elements and compounds as a starting material for the production of many commercially important nitrogen compounds. Hydrazine is an inorganic compound with the chemical formula H_2NNH_2 (also written N_2H_4). It is a colorless

flammable liquid with an ammonia-like odor. Hydrazine is highly toxic and dangerously unstable unless handled in solution.

2 Technology of experiment

The schema of experimental arrangement to demonstrate what steps were made to investigate the gas state is shown in Fig. 1. The device, which can be used also as a proportional counter, is cylinder (1) in appearance with removable top and bottom plates to facilitate rearrangement of the wire and plate anodes as desired. The top of the cylinder (1) contains an aluminum foil window (2). The plate anode (3) (beryllium 0.5 mm) is used for obtaining a uniform electrical field in gas space. Mossbauer radiation passes through the window (2) all time Beryllium anode (3) is connected through the high voltage (HV) connector (5) to HV source to obtain a uniform electrical field and gas discharge. The wire anode (4) is a special wire spaced four- five mm apart from the absorbent (7). The wire anode (4) is connected through the high voltage (HV) connector (5) to the HV source. Before interaction of gas with the absorbent (7) its spectrum is registered. For this goal the faucets (9) and (11) are opened.

The accelerated ionized molecules hit the absorbent and interact with iron on the absorbent surface. The time of discharge depends on many factors and can vary from some minutes up to 10 hours. Then the analyzed gas is pumped out, the faucet (13) is closed, the faucets (11) and (10) are opened and after removing from the previous gas from the counter, the He gas flow rate is maintained at approximately 3 cm^3/min. The new spectrum of absorbent is registered. This spectrum shows the result of gas interaction with iron on the surface of the absorbent. The absorbents are the thin films of ^{57}Fe on the surface of various substrates.

The used Mossbauer spectrometer operated in the mode of constant acceleration. ^{57}Co (Cr) was used as a source of resonant radiation. Isomer shifts are given relating to metallic iron. The fitting of spectra is carried out using programme Univem MS.

Interaction of the gases was carried out with the thin films of ^{57}Fe on the surface of various substrates (absorbents), in particular, on substrates from aluminum, glass and beryllium and with massive metal. It was experimentally proved that the changes of spectra of massive samples are very small. The greatest changes in the shape of spectra are noticed on thin iron films. The usage of dielectrics as substrates leads to the decrease of gas interaction with the surface of iron films. The Mössbauer spectra of paramagnetic phases were observed in case of very little thickness of iron films. The parameters of these spectra may coincide with the parameters of spectra of the phases that are formed under gas influence. This can complicate the interpretation of the paramagnetic phases formed under the gas influence. It was experimentally proved that the most acceptable thickness is (400-500 Å). This conclusion results from the analysis of iron films spectra of conversion electrons Mössbauer spectra (CEMS) of initial ^{57}Fe films and films treated by gases (Fig. 2).

The analysis showed distinctions in interaction of vapors of liquid ammonia and hydrazine. The spectra differ by values of isomer shifts and the quadrupole splitting of the compounds formed on ^{57}Fe films.

Thus, the usage of the resonant absorption and CEMS gives the possibility to carry out identification of gas molecular state.

The gases poorly interact with iron. A special camera and a technique were developed for the acceleration of this interaction. The essence of the technique consists in the acceleration

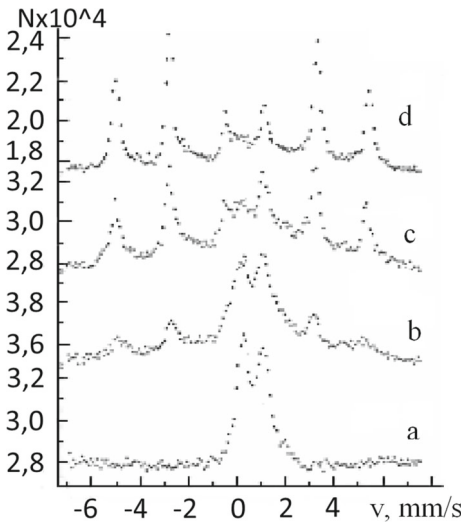

Fig. 2 Mössbauer spectra of ^{57}Fe in thin films, obtained by thermo vacuum condensation on aluminum foil: **a**-90 Å; **b**-150 Å; **c**-270 Å; **d**-400 Å

of ions of gas molecules in the electric field. The usage of the specified technique allowed to obtain insight on the interaction of iron films with the complex gas compound.

3 Results and discussion

Results of the analysis are shown in Fig. 3. It is known that superficial interactions take place through the following stages: adsorption of atoms on the surface of the active agent, the fixing of the adsorbed atoms and their interaction (chemical and diffusion) with the material of the active agent. If the speed of condensation is less than the speed of diffusion of gas atoms, a diffusion layer is formed on the surfaces of the active agent. The structure and thickness of the diffusion layer are defined by diffusive mobility of atoms in the material of the active agent.

Results of investigation ammonia (NH_3) gas are shown in Fig. 3. Before the gas influence the spectrum of thin iron layer enriched with ^{57}Fe is like spectrum of pure massive iron (Fig. 3 a). The central part of the spectrum (Fig. 3 b) is changed by the influence of discharge in NH_3. The lines of quadrupole splitting of paramagnetic phases appear. The parameters of the lines are the following: isomer shift IS $= 0.325 \pm 0.025$ mm/s, quadrupole splitting QS$=0.969 \pm 0.025$ mm/s. According to the values of IS and QS it is possible to conclude that the compounds of iron atoms with nitrogen and perhaps with hydrogen were formed. In this compound iron atoms are in a trivalent state. The next experiment was made with N_2H_4. The interaction with the gas N_2H_4 in similar conditions results in spectrum changes also. The lines of quadrupole splitting of paramagnetic phases appear too, but with other parameters. In this case IS $= 0.472 \pm 0.030$ mm/s, QS $= 0.885 \pm 0.030$ mm/s. The iron atoms in this phase are in another state. QS decreased, IS is rather displaced to the area of the bivalent state of iron. As there are the same atoms in both compounds, namely atoms of hydrogen and nitrogen, distinctions in chemical shifts can be explained only with the distinction in interaction of different molecules of these gases.

Thus, these experiments testify that by means of CEMS it is possible to create techniques for the identification of a gas molecular state.

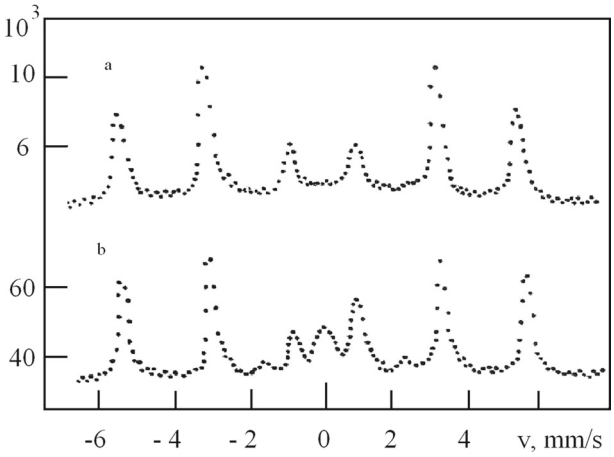

Fig. 3 Mössbauer spectra of ^{57}Fe in thin films of iron on an aluminum substrate: **a** in the initial state; **b** after treatment in the gas discharge NH_3

4 Conclusions

It is shown:

1. That resonant scattering on the basis of registration of conversion electrons can be used for the identification of a gas molecular state.
2. The optimum thickness of iron -57 films are 400-500 angstrom. The process of interaction of the studied gas with the active agent is accelerated by an electric discharge in gas.
3. The most effective active agent is the dusting of iron films on metal foils.

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