APPLICATION OF SEMICONDUCTOR METHOD TO ANALYSIS OF PHOTOCHEMICAL REACTIONS WITH THE PARTICIPATION OF CHLORINE AND ITS COMPOUNDS WITH OXYGEN

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The interaction between the OClO *and* In_2O_3 *in the temperature range* 260–350°C *has been investigated, as well as the interaction of chlorine atoms with* ZnO. *Regularities in the change of* In_2O_3 *conductivity at* OClO *adsorption in the range of* OClO *concentration from* 0.03 *to* 1 ppm *have been revealed, as well as the regularities of* ZnO *conductivity change due to adsorption of chlorine atoms. Kinetics of* In_2O_3 *and* ZnO *conductivity change has been studied. Demonstrated is the possibility to apply the method of semiconductor sensors (SCS) to detection of atomic and molecular chlorine, as well as* ClO_x *compounds in the atmosphere and to study the photochemical and heterogeneous processes with the participation of chlorine or its compounds.*

INTRODUCTION

As known, one of the causes of ozone layer destruction is the effect of chlorine compounds that becomes more intense in the presence of stratospheric clouds. It is related to heterogeneous chemical reactions running on their surface. Products of such reactions: molecules Cl_2, ClO_2, HOCl, under UV solar irradiation dissociate with the formation of Cl and ClO that actively interact with the ozone. Among the latter, of great interest is the chlorine dioxide having two isomeric forms: symmetric stable radical OClO and unstable superoxide radical ClOO being the active participants of the atmospheric chlorine cycle.[1–7]

Superoxide radical ClOO is formed as an intermediate product of molecular chlorine photolysis in the presence of oxygen[2]:

$$Cl_2 + h\nu \to 2Cl \ ;$$

$$Cl + O_2\, M \leftrightarrow ClOO + M \ ;$$

$$ClOO + Cl \to 2ClO \ , \qquad (a)$$

$$ClOO + Cl \to Cl_2 + O_2 \ , \qquad (b)$$

as well as in OClO isomerization under UV irradiation in an isolated inert matrix[3]:

$$OClO + h\nu \to ClO + O \ ,$$

$$ClO + O \to ClOO \ .$$

OClO isomer is sufficiently well studied due to its wide use as a bleaching and disinfecting mean in pulp industry and in water cleaning.[8,9] Under UV irradiation in vacuum and in air, OClO dissociates in two ways[5]:

$$OClO \xrightarrow{360\ nm} OCl + O \quad \Delta H = -48\ kJ/mole;$$

$$OClO \xrightarrow{360\ nm} Cl + O_2 \quad \Delta H = -154\ kJ/mole, \qquad (1)$$

and probability of the first reaction is 85%, while for the second one it is 15% (Ref. 5).

Different analytical methods are developed for the detection of OClO. Among them there are spectrometric, electrochemical, iodometric, colorimetric, and other methods capable of measuring low concentrations of OClO in liquids,[8,9] but these methods are poorly applicable to atmospheric measurements. Under laboratory conditions, to study photochemical processes with the participation of chlorine and its compounds with oxygen, UV, IR, and Raman spectroscopy are used, as well as photoionic mass-spectrometry and resonance fluorescence.[2,3,6,7,10] In the atmosphere, absorption spectroscopy in the visible and UV ranges is used for determining OClO concentration,[1,11,13] and resonance fluorescence is used for determining the concentration of ClO.[12] The above methods are selective and sensitive, but the complexity and very expensive equipment hamper their use. Therefore, there is a need for more simple and cheap methods of monitoring the atmospheric impurities.

The method of semiconductor sensors (SCS) seems to be promising for detection and study of physico-chemical properties of different trace molecular species, short-living atoms, and radicals.[14] It has many advantages over electrochemical, optical, and other methods, because the semiconductor sensors are highly sensitive, having fast response and small size, and they are cheap. In addition, they are sufficiently chemically resistant, thermally and mechanically stable. The development of selective sensor is rather complex, but there are some ways to solve this problem: selection of temperature range for detection, alloying of sensor surface, application of different filters, use of multicomponent sensors, construction of neuron networks, preactivation of molecule in gas phase by thermal, catalitic or UV impact resulting in its excitation or decay into more active components.[14,15]

The SCS method is based on the change of semiconductor electrophysical characteristics under contact with the environmental components. There is three types of the method: equilibrium, kinetic, and continuous.[14] In the first case a sensor is placed into the medium under study, stationary level of its conductivity is measured. In the second case the sensor is in air flow, into which a portion of studied gas is injected, and the initial rate of the conductivity change is measured. When using the continuous method a sensor is constantly in the gaseous medium analyzed, and changes in the semiconductor conductivity serve as the indication of changes in the gas species concentration in the medium. In this case, some calibration parameters (constants of adsorption, desorption, and equilibrium) should be predetermined, while the current value of the electric conductivity and the rate of its change are the parameters to be measured.

The SCS method is convenient for use both in laboratory conditions, and for continuous *in situ* analysis under laboratory conditions. Industry of a number of countries produces semiconductor sensors for detection of CO, CH_4, H_2S, NO_x (Ref. 16). In addition, the method is widely used in the experimental studies of physicochemical processes, such as recombination of atoms (H, O, N) and radicals (methyl, NH_2, NH), pyrolysis of gases (O_2, N_2, H_2, Cl_2, acetone, CO_2, etc.) on hot filaments, photolysis in gaseous medium (ethylene, acetone, NH_3, O_2, N_2, CO_2) with the following analysis of photolysis chemical products, photolysis of AgCl, emission of active particles (atoms of hydrogen, oxygen, silver, alkyl radicals) from surface of solid bodies, etc.[14–18]

It should be noted, however, that literature data on kinetics and mechanism of chlorine interaction with semiconducting metal oxides are only few in number,[17–20] while the data on the mechanism of ClO_2 adsorption on surface of a solid body are practically absent. In Refs. 19–21, it is shown that a semiconductor sensor on the base of In_2O_3 with the addition of other metal oxides is highly sensitive to chlorine. Only one paper is known about the application of such a sensor to measuring ClO_2 concentration in water solutions.[22]

This paper demonstrates the possibility of SCS method application to detection of chlorine atoms, OClO, and ClO_x in vacuum and air.

EXPERIMENT

The sensor is a polycor substrate (Fig. 1) with a platinum heater on one its side (*1*) and sensitive layer on the other one (*2*). As a sensor's sensitive layer we used indium oxide In_2O_3 with additions of Fe_2O_3 and zinc oxide, ZnO.

The OClO was produced in due to interaction of $NaClO_2$ solution with a weak solution of HCl or gaseous chlorine. Thus produced gas was identified in UV and IR spectra. The OClO concentration was monitored by the photocolorimetric method. Experiments were conducted in flowing-injection setup at OClO concentration ranging from 0.03 to 1 ppm in air.

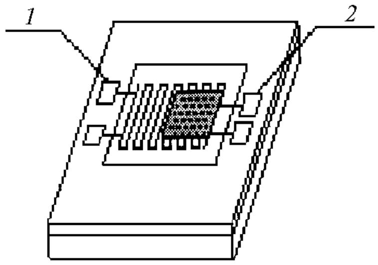

FIG. 1. External appearance of the sensor.

Chlorine atoms in the absence of chlorine molecules in the gas phase were produced by photolysis of AgCl films with DRSh lamp.[18] Experiments were done in a vacuum chamber combined with a mass-spectrometer.

DISCUSSION OF THE RESULTS

Adsorption of the chlorine dioxide leads to decreasing of the conductivity of semiconductor oxide In_2O_3, alloyed with Fe_2O_3. Figure 2 shows the kinetic of the sensor conductivity change at OClO adsorption in relative units, where σ_0 and σ are the initial and current values of the conductivity. As seen from the figure, at optimal temperature (260–350°C) of the

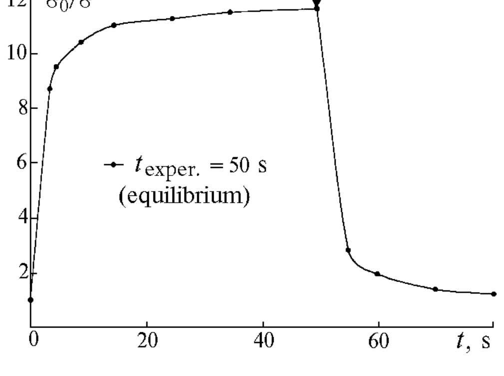

FIG. 2. Kinetic of the sensor conductivity change at chlorine dioxide adsorption under optimal temperature of the sensor operation [OClO] = 270 ppb.

semiconductor the sensor has good enough dynamic characteristics: response time (less than 1 s), time of the equilibrium establishment (15 s), relaxation time (20 s) that is comparable with the analogous parameters for the ozone sensor of similar composition.[21] The proportionality was established between the concentration of OClO in the gas phase and electrophysical response of the sensor in kinetic and equilibrium modes of operation: it is linear for the initial rate of the sensor conductivity change and power for equilibrium value of the sensor conductivity (Fig. 3) described respectively by the equations

$$\frac{d\sigma}{dt} = k\,[\mathrm{ClO_2}]\,, \tag{2}$$

$$\frac{\sigma_0}{\sigma} = K\,[\mathrm{ClO_2}]^x, \tag{3}$$

where k is the adsorption constant; K is the equilibrium constant; x is the exponent depending on the gas nature and semiconductor composition.

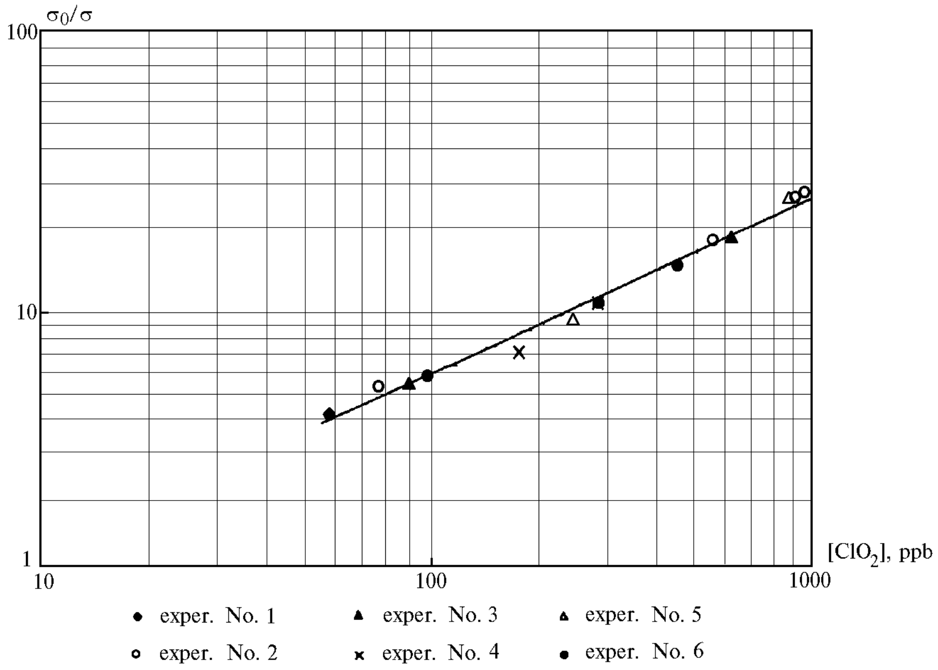

FIG. 3. Stationary value of the sensor conductivity change vs chlorine dioxide concentration at the sensor temperature of 300°C.

In our experiments $x = 0.83$ that coincides with data[22] for the sensor of analogous composition calibrated against OClO concentration in water. The limited range of OClO concentration measurable with the sensor was obtained by extrapolation of Eq. (3) to signal value at 20% level (Fig. 3), and it is ≈20 ppb ($5\cdot10^{11}$ cm^{-3}).

The sensor sensitivity increased due to the use of UV radiation for preillumination of analyzed gas flow before it comes to the sensor operating in the dark mode. In this case, the additional and significant signal of the sensor conductivity change of the donor-acceptor type (Fig. 4) was observed against the background of the sensor conductivity change due to OClO adsorption. This signal is indicative of the competitive processes that take place on the sensor surface. The acceptor signal is likely related to the additional chemosorption of active particle-products of OClO photolysis (scheme 1) or products of secondary reactions. The donor signal can be explained by the interaction of gas-phase particles with the adsorbed layer similarly to the case of Cl-atoms adsorption on the semiconductor – metal oxides in the presence of chlorine molecules[17] or transfer of excitation, for example, vibrational, from adsorbed particles to the solid body. The latter assumption is supported, for example, by ClO production by reaction (1) in vibrationally excited states.[5] The nature and energy state of particles adsorbed on the sensor surface in photolysis of air medium containing OClO, as well as the mechanism of their interaction with the sensor surface should be the subject of further research. However, the fact of 35 fold increase of the acceptor signal of the sensor (Fig. 4) will enable the decrease in the limited detectable OClO concentration in air down to 330 ppt ($8\cdot10^9$ cm^{-3}) that is comparable with the OClO concentration in the Antarctic – $5\cdot10^{10\pm1}$ cm^{-3} (Ref. 1).

Significantly lower concentrations of chlorine atoms were detected in vacuum conditions at AgCl photolysis in the absence of chlorine molecules in the gas phase.[18] Emission of chlorine atoms from AgCl surface under exposure to UV radiation was supported by the intercomparison of the molecular chlorine mass spectrum with the mass spectrum obtained at AgCl photolysis, as well as by comparison of signals of the combined sensor – thin film and crumbly ZnO tablet operating based on the principle of different behavior of the atoms and molecules in the adsorbent vapor. The absence of tablet signal, as well as 70th mass, and, on the contrary, the presence of tablet signal and appearance of 35th mass in AgCl photolysis were indicative of the presence of chlorine atoms in the gas phase. The flow intensity of Cl atoms emitted by AgCl was estimated based on the photometric measurements of power of incident (10^{15} quanta/s) and transmitted through AgCl ($9\cdot10^{14}$–$9.9\cdot10^{14}$ quanta/s), UV radiation, taking the value of radiation scattered by polycrystal samples of AgCl being an order of magnitude greater than the absorbed radiation.[18,23]

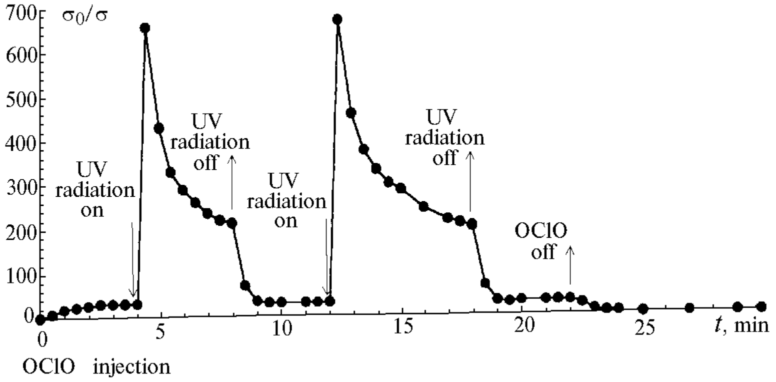

FIG. 4. Kinetics of the sensor conductivity change at adsorption and photolysis of the OClO. [OClO] = 730 ppb. *Sensor temperature is* 300°C.

AgCl sample absorbs 10^{12}–10^{13} quanta/s depending on the film thickness and degree of AgCl dechlorination, that within one order of magnitude coincides with the value of the absorbed radiation calculated by the Lambert-Beer law for AgCl film 10^{-5}–10^{-4} cm thick. For the basic lines of DRSh–250 lamp in the AgCl absorption of the band at $\lambda = 360$ nm (100%) and $\lambda = 313$ nm (65%) the AgCl absorption coefficient was taken equal to 10^4 cm^{-1} and $2\cdot10^3$ cm^{-1}, respectively.[23] Intensity of clorine atom flux from AgCl film surface is $5\cdot10^{11}$ – $5\cdot10^{12}$ cm$^{-2}\cdot$s^{-1} with quantum efficiency taken as 0.5.[23]

A share of chlorine atoms falling on ZnO calculated from the geometry of the experiment is $3\cdot10^{-3}$, consequently the intensity of the chlorine atoms flux is 10^9–10^{10} cm$^{-2}\cdot$s^{-1}.

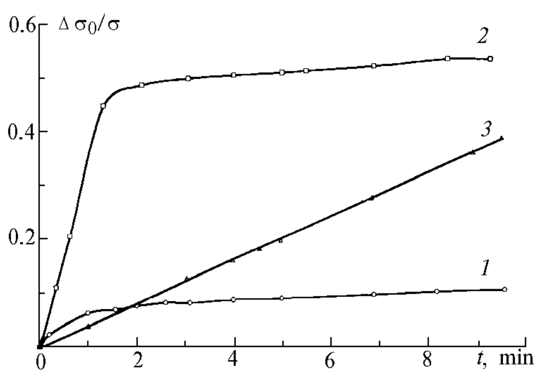

FIG. 5. Changes of the relative conductivity of ZnO *film due to chemosorption of chlorine molecules (1, 2) and atoms (3) at* 25°C: $[Cl_2]_v = 1\cdot10^{10}$ cm^{-3} *(1)*, $[Cl_2]_v = 1\cdot10^{12}$ cm^{-3} *(2)*; $[Cl_2]_v = 10^5$–10^6 cm^{-3} *(3)*.

Figure 5 compares the changes in the relative conductivity $\Delta\sigma/\sigma_0$ of ZnO film at chemosorption of atoms (curve *1*) and molecules (curves *2*, *3*), where $\Delta\sigma$ is the change of the film conductivity in the process of adsorption. It follows from Fig. 5 that signals of ZnO conductivity change $\Delta\sigma/\sigma_0$ due to adsorption of chlorine atoms and molecules are the values of the same order under conditions when the concentration of chlorine atoms near ZnO film is six orders of magnitude less than the concentration of chlorine molecules. Such a result is indicative of a significantly greater (by several orders of magnitude) value of adhering coefficient and ionization coefficient of chlorine atoms as compared to the corresponding coefficients for chlorine molecules.

CONCLUSION

Semiconductor sensors can be used for detecting molecular and atomic chlorine and chloroxide radicals. Use of the semiconductor method to study photochemical and heterogeneous processes with the participation of chlorine and its oxygen compounds, as well as to monitoring of atmospheric impurities containing chlorine seems to be much promising.

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