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Hysteresis in resistance isotherms as a function of moisture for porous glass with conductive nanoparticles

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Moisture adsorption-desorption by silica porous glass wafer with a built-in conductive phase on the graphite base was investigated. The phenomenon of hysteresis was discovered in the dependence of the resistance of porous glass on changes in ambient temperature. An explanation of this phenomenon was proposed. The temperature ranges for its minimization were estimated. The ways of intellectualization of such kind of sensors using microprocessor techniques was demonstrated. The usage areas of such sensor were specified.
Keywords: humidity sensors, porous silica glass, sorption hysteresis.

Гістерезис ізотерм залежності опору шпаристого скла із провідною фазою з наночастинок від вологості. *Я.І.Лепіх, І.К.Дойчо*

Досліджено абсорбцію-десорбцію вологи пластиною силікатного шпаристого скла із вбудованою провідною фазою на ґрафітовій основі. Виявлено явище гістерезису залежності опору шпаристого скла при зміненні температури середовища. Запропоновано пояснення цього явища і виявлено температурні межі для його мінімізації. Продемонстровано можливість інтелектуалізації сенсорів такого типу шляхом використання мікропроцесорної техніки. Визначено сферу використання такого сенсору.

1. Introduction

Traditional capacitive humidity sensors require the use of complex technological processes to form the sensing parts of various types that intersect, but do not come into contact with each other. This is a condition for the functionality of the sensor in a wide range of humidity [1]. The porous silicate glass contains a system of interpenetrating cavities of various sizes ranging from 10 to more than 100 nanometers [2]. Therefore, due to the very design of the slot plate, there will always be a system of slots inside it, the dimensions of which are suitable specifically for a given humidity range. However, an ordinary sample of sponge silicate glass cannot play the role of an active element of a resistive humidity sensor. Firstly, the significant surface roughness of the corresponding plate does not allow creating ohmic contact with it even with the help of conductive paste [3]. Secondly, a plate made of silicate slotted glass has a very high intrinsic resistance (up to hundreds of TOm), against the background of which the influence of environmental humidity will remain almost unnoticeable.

In this work, the task was to identify and investigate the possibility of using porous silicate glass as a sensitive element of a humidity sensor in order to improve its metrological and constructive-technological characteristics. The dependence of the sensor characteristics on temperature was studied, which is fundamentally important for a humidity sensor of any type.

2. Results and discussion

The principle of operation of the resistive humidity sensor is based on the property of porous or powdery conductive materials to change their electrical resistance under the influence of environmental moisture. The active element of a humidity sensor of this type has a number of advantages compared to those used in traditional capacitance sensors due to the availability of the material and the simple technology of creation without the use of expensive and cumbersome devices. The technology of creating plates of porous silicate glass of various types is described in [2, 4]. Samples obtained using this technology are subjected to additional processing, namely, saturation of porous silicate glass with a glucose solution, followed by low-temperature annealing [5-7]. Glucose is regenerated to carbon in the form of graphite and forms a conducting phase in the gaps of the matrix in the form of an ensemble of nanoparticles thereby reducing the intrinsic resistance of the plate by almost 2 orders of magnitude. Using a mask, you can create zones with a high concentration of graphite [7] at the ends of the plate to reduce the surface roughness and provide ohmic contact with the sensing element. An important advantage of this material is its ability to work in a fairly wide range of temperatures, from close to room temperature to negative ones. The latter is due to the fact that at negative temperatures, humidity is determined by the number of water molecules sublimated into the air. Entering the cavities of the porous plate from the environment, these molecules form an ensemble of water nanoparticles. In this state, water molecules do not interact with each other, therefore, they do not form ice, which settles on the wick of aspiration hygrometers, rendering them inoperable at subzero temperatures. Resistance isotherms depending on ambient humidity for a porous silicate glass plate are shown in Fig.1. It can be seen that with increasing humidity, the resistance of the plate also decreases, since an additional conducting phase of water molecules is gradually formed inside it. In addition, the isotherms practically do not differ from each other under different operating conditions (which do not destroy the sample) at experimental temperatures in full accordance with the previously obtained results [7-8]. This applies, at least, to the temperature range from -20°C to 30°C. The specified curves are the result of thermodynamic equilibrium between water particles that determine air humidity and an ensemble of nanoparticles inside the pores. The conditions for such equilibrium are maintained at different temperatures. This fact is associated with a simultaneous increase in the number of water molecules outside the active element of the sensor and inside the pores with increasing humidity, regardless of temperature and with a stable configuration of a particular porous sample.

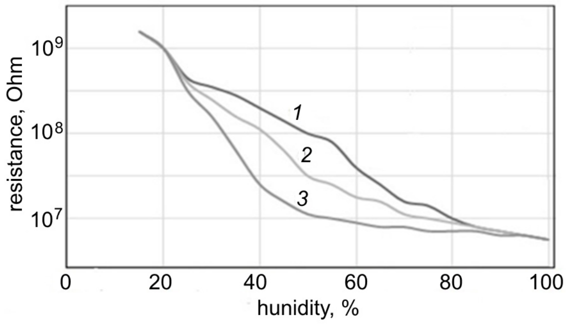

Fig. 1. Electrical resistance isotherms depending on ambient humidity for porous glasses:1 – change in humidity in the temperature range from -20°C to 30°C; 2 – decrease in humidity at a temperature of 40°C; 3 – decrease in humidity at a temperature of 60°C

With a further increase in ambient temperature to values significantly above room temperature, isotherms depend on the direction of change in humidity. If the humidity of the environment increases, the corresponding curve remains the same as it was at lower temperatures [8], but when the humidity decreases, the isotherms branch out with the appearance of the so-called sorption hysteresis. This is due to the formation of menisci from water particles in small cracks [9] which got there when the plate was saturated with moisture. At high temperatures, a decrease in the humidity of the environment leads to a very rapid decrease in the amount of water outside the sample, while inside the cracks, the release of water molecules occurs more slowly due to the presence of the specified menisci. The resulting delay effect slows down the release of the plate from moisture, so the same humidity will correspond to an underestimated value of the plate resistance, which is clearly seen from Fig. 1. It can be seen that if the specified delay at 40°C is insignificant, then at 60°C it is already quite significant, and this effect will be stronger, the higher is the air temperature. Therefore, when the humidity decreases, for each temperature it is necessary to construct two corresponding separate branches of the sorption hysteresis of the dependence of resistance on humidity. In this regard, the use of sensors of this type to control humidity in tropical climate will require compensating devices with microprocessor technology, which, depending on the direction of humidity change, would automatically switch the humidity sensor to the required hysteresis branch. These devices currently do not pose a technical problem and are inexpensive. In addition, such devices can also perform certain service functions, which make sensors intellectualized and expand the scope of their application. The specified hysteresis effect does not significantly affect the operation of the resistive humidity sensor in temperate climate, since it is observed only at temperatures significantly higher than room temperature. At the same time, a significant advantage of sensors of this type is the ability to work at low temperatures, including negative ones, which allows them to be used, for example, in agriculture to maintain the necessary conditions in vegetable storehouses, etc.

3. Conclusions

Porous silicate glass with an embedded conducting phase of an ensemble of carbon graphite nanoparticles is a moisture-sensitive system, so it can be used as a sensitive element of a resistive humidity sensor.

The resistance of this system depends on the direction of change in the ambient humidity and the corresponding isotherms have sorption hysteresis. Moreover, in the case of an increase in humidity, the isotherms are practically independent on the ambient temperature (within temperatures that do not destroy the system); while in the case of a decrease in humidity, the dependence on temperature becomes significant. At temperatures not exceeding 30°C, the hysteresis branches completely coincide, and at higher temperatures, they branch out.

An important advantage of humidity sensors of this type is their ability to work at negative temperatures and the possibility of their intellectualization using microprocessor technology.

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