Gas-sensing properties and modeling of silver doped potassium hollandite

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ABSTRACT

In this paper the gas sensing properties of Ag–K-hollandite prepared by K–Ag ion exchange are investigated. The proposed material was used as the active layer of micromachined conductometric gas sensors and tested in different environmental conditions with a number of target gases such as CO and NO_x. The response to test gases was evaluated in a temperature interval from 200 to 350 °C where surface phenomena can completely explain the sensor behavior. The proposed material was studied also by means of XPS and thermal analyses. The investigated material is a p-type semiconductor and shows a reproducible response and a complete recovery. Data obtained are discussed and a model based on surface states describing the material behavior is proposed.

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1. Introduction

Hollandite, $(\square,M)_2Mn_8O_{16}$, is an octahedral molecular sieve, composed of edge-sharing MnO_6 octahedral double chains, which are corner connected to form a 2 × 2 tunnel with a pore diameter of 5.1 Å (Fig. 1). The tunnels are partially filled with cations (M = K, Na, Ag, Ba, . . .) that may have a high mobility due to their weak interaction with MnO_2, and that can be easily interchanged with other ions. The octahedral sites are occupied by Mn^{4+} along with some Mn^{3+} to compensate for the positive charge of the tunnel ions [1–5]. The ability for ion-exchange and the mixed valence of manganese of this unique class of inorganic materials offer the opportunity for tuning the physical and chemical material properties by controlling the number and kind of ions in the tunnels. For example, partial exchange of K^+ ions in the tunnels with H_3O^+ ions yielded excellent acid catalysts for selective oxidation reactions [6], while exchange with Cs [7] and Ag [8–10] produced materials with novel catalytic, structural or electric properties. This material behaves as a semiconductor, and it was proved for MnO_2 that the electric conduction is mainly determined by the chemisorption/desorption of oxygen

ions in molecular and atomic form [11]. Moreover there are several studies which indicate that this material has exceptional catalytic properties for CO and VOCs oxidation [7,12–16].

Taking into account these results reported in the literature, in this paper the gas sensing properties of Ag-exchanged K-hollandite are studied, focusing on Ag–K-hollandite suitability to operate as the active layer in conductometric 'surface-type' sensors.

The most used and studied conductometric metal oxide sensors are those for which the sensing mechanism is controlled by gas-surface reactions ('surface-type sensors'), while the bulk properties of the material, at the operating temperature, can be considered constant and independent from the chemical environment [17]. In this case it is possible, in fact, to obtain a large sensitivity and a fast response, together with lower operating temperatures. The sensor response entirely depends on the adsorption and desorption of gases at the surface, followed by the transfer of electrons from the oxide surface to the adsorbates or vice versa. The resistance value, at least for poorly sintered films, is mainly determined by the magnitude of the electric field built up at the surface by the charge localized on the adsorbed ions: for instance, in a porous grained film, by the potential barrier, which is present between adjacent grains.

Summarizing for this kind of sensors, the sensing mechanism is related only to those chemical reactions, which cause the trapping

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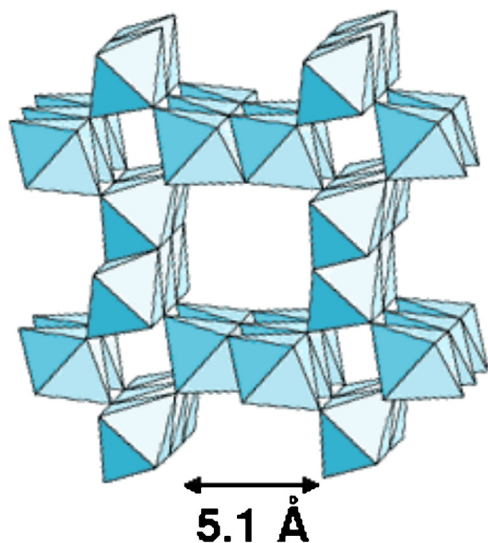
Fig. 1. Basic motive of the hollandite ($\square$,M)$_2$Mn$_8$O$_{16}$ framework structure, characterized by a tunnel that displays two sites per every eight Mn atoms to host alkali atoms or molecules up to about 3 Å in diameter. The guest atoms are normally charged (e.g. K$^+$) requiring that an equivalent amount of Mn^{4+} passes to the trivalent state.

Fig. 2. SEM microphotograph showing sensor film after drying.

or releasing of carriers, the formation of an electrical field on the material surface or, in other words, the creation of a surface layer with a modified carrier density [18–20]. All these phenomena, due to different effects and in relation with the material microstructure, can influence the electron conduction. On the other hand, the oxidation or reduction of a gas, which does not imply charge transfer from the sensor bulk or surface, does not play a role in the sensor response. This can happen, for example, if neutral adsorbed oxygen is responsible for the gas oxidation.

This paper aims at the experimental study and modeling of these specific aspects of the material behavior, related to the development of 'surface-type' chemoresistive sensors.

2. Materials and methods

2.1. Material and sensor preparation

The Ag-exchanged hollandite used for this study has been prepared following De Guzman et al. [21] for the reflux synthesis of K-hollandite (cryptomelane) and Li and King [22] for K–Ag ion exchange in aqueous AgNO$_3$ as detailed in an earlier work [23]. The chemical composition of this compound, as ascertained from Rietveld refinement, X-ray fluorescence and X-ray photoelectron spectroscopy, comes near to ($\square_{1.2}$Ag$_{0.5}$K$_{0.3}$)Mn$_8$O$_{16}$ with some indications that the number of tunnel cations might be slightly depleted in the surface region of the grains. The size of the crystallites is ~14 nm indicating that the surface makes up an important part of the material (~125 m^2/g). The crystal structure, as revealed by Rietveld refinement [23], shows that Ag and K occupy two different sites in the tunnel with coordination numbers 4 and 8, respectively.

A suspension of finely ground powder in water, with the addition of dimethylphthalate as a binder, was used to prepare thick films by drop coating on micromachined silicon substrates Mic-3000i (Microsens-CH) equipped with gold electrodes and poly-Si heaters. The active sensing area of these devices is ~300 μm across, and the distance between the interdigitated electrodes is ~15 μm. The deposits were then dried and heated to volatilize the binder (bp 284 °C).
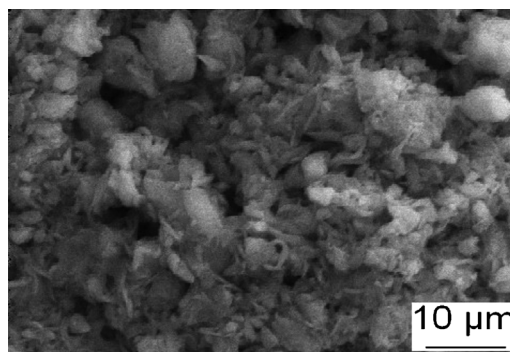
Optical microscopy using a standard petrographic microscope (Leica DM LSP) and an attached photocamera was used, together with secondary electron microscopy (SEM, Philips XL30), to control integrity and morphology of the deposited films down to ~100 nm resolution.

It can be seen from Fig. 2 that the porous films, obtained as described, consist of large loosely bound grains (some μm in diameter) of semiconductor. In these grainy layers, it is expected that the dominant effect determining the sensor response is the variation of the surface charge density due to the adsorption and ionization of gases.

2.2. Material characterization

Thermogravimetric and differential thermal analyses were perfomed on a TA Instruments Q600 equipment coupled with a Pfeiffer Thermostar quadrupole mass spectrometer for the analysis of evolved gases.

X-ray photoelectron spectra (XPS) have been obtained for both the pristine material and the sensor surface after exposure to different gas flow regimes. XPS spectra were recorded under ultrahigh vacuum conditions in a chamber equipped with a hemispherical electron energy analyzer (VSW HA100) and a non-monochromatized Al Kα (1486.6 eV) X-ray source. The X-ray gun was operated with a power of 180 W. The electron take off angle was 90°. Low-resolution survey spectra were collected in an electron kinetic energy range from 400 to 1490 eV with a constant pass energy of 90 eV. Higher-resolution spectra were acquired for the most relevant peaks with a constant pass energy of 44 eV. The analyzed area was a circle of 5 mm in diameter. the binding energy (BE) scale was calibrated setting the aliphatic carbon component of the C 1s peak (as determined by the curve fitting analysis) to 285.0 eV. For the quantification of the XPS intensities, we used the atomic sensitivity factors reported in [24].

The gas sensing properties of Ag-exchanged hollandite were assessed by means of the measurement system described in [25], developed to simultaneously characterize up to 8 sensors mounted in an array. This system is able to individually control the temperature of each sensor with a 5 °C temperature accuracy for temperatures higher than 250 °C. The temperature control system is based on a microcontroller implementing a control cycle of 100 μs.

The gas-dispensing unit is a digitally controlled line providing the possibility to inject the desired gas or gas mixture into the measurement chamber, and to control the gas flow (up to 500 mL/min) by means of three mass flow controllers. A bubbler containing pure water in a thermostatic bath allows to set the desired relative humidity (RH) of the mixture sent to the measurement chamber. This latter is kept in an incubator at 25 °C. RH