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Electrical Properties of Thin-films of the Mixed Ionic-electronic Conductor CuBr: Influence of Electrode Metals and Gaseous Ammonia

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Abstract

The electrical properties of sputtered thin-films of CuBr are measured using gold or copper electrodes and in presence of ammonia. The I–V characteristics are strongly dependent on the choice of the electrode metal: an ohmic response is observed with copper electrodes, which act reversibly for ion exchange, but exponential dependencies are measured with blocking gold contacts. An increase of the film resistance is observed in presence of ammonia: the response time is very short and the signal is reversible. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Solid state gas sensors play a fundamental role for environmental protection, including automotive exhaust gas analysis and control of industrial combustion processes. The development of intelligent devices with sensing, computing and actuating subsystems is a major technological challenge. Electrochemical detectors are very useful, given that chemical changes are directly converted into electrical signals. Thin-films of active sensor materials connected to micro-electronic circuitry can be the basis of miniaturised sensing devices.

Copper(I) bromide CuBr is a mixed ionic–electronic conductor with predominant ionic conductivity above 200°C.[1,2] A p-type semiconductivity was found at ambient temperature by Hall effect measurements and Mott–Schottky analysis.[3–5] Thin-films of CuBr are candidate materials for electrochemical gas sensors, given that mixed conductivity leads to faster response and suitability for ready integration into electronic devices.

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We have prepared thin-films of CuBr on different substrates by r.f sputtering.[6] Structure and composition of the films were investigated by optical and electron microscopy, X-Ray Diffraction and X-Ray Spectrometry (EDX). The electrical properties were studied *ex–situ* by two-point d.c. current-voltage measurement.[6,7] In continuation of this work, we present here the influence of model electrode metals, reversible or blocking for ion exchange, on the I–V characteristics of CuBr films.

It is well known from aqueous chemistry that copper ions form very strong complexes with ammonia (NH_3).[8] Based on an analogy of solution and gas phase chemistry, we expect a strong attraction between ammonia gas and mobile copper ions in the solid phase and, consequently, conductivity effects due to interfacial layers. First experiments on the sensor characteristics of CuBr films for ammonia gas at ambient temperature are presented.

2 Experimental

The details of the r.f. sputtering procedure can be found in our previous paper.[6] Different electrode arrangements were used to study the I–V characteristics. For ex-situ measurements, cylindrical gold or copper electrodes of 1 mm diameter were evaporated on top of the CuBr thin-films previously deposited on metallic substrates.

The in-situ d.c. characteristics were measured inside the deposition chamber (i) under dynamic vacuum and (ii) in presence of a certain NH_3 partial pressure. The pressure inside the chamber was measured by a MKS 122B capacitive gauge with an uncertainty of ± 1 mbar. The CuBr films were deposited on inter-digited copper electrodes previously made by evaporation on glass substrates. The advantages of this type of structure are robustness, versatility and easiness to reproduce using photo-lithographic masks.

3 Results and Discussion

3.1 Reversible and blocking metal electrodes

Figure 1 shows typical I–V characteristics of CuBr thin-films with two gold electrodes (Au/CuBr/Au structure, curve A), two copper electrodes (Cu/CuBr/Cu, curve C) and one copper/one gold electrode (Au/CuBr/Cu, curve B). Whereas the characteristic with two copper contacts is ohmic, clearly non-linear responses are observed with one or two gold electrodes. A consistent interpretation of these results is based on the assumption that copper electrodes are reversible ionic probes, whereas ionic current is blocked by use of gold and that the exponential dependencies are due to Hebb–Wagner polarization.[9]

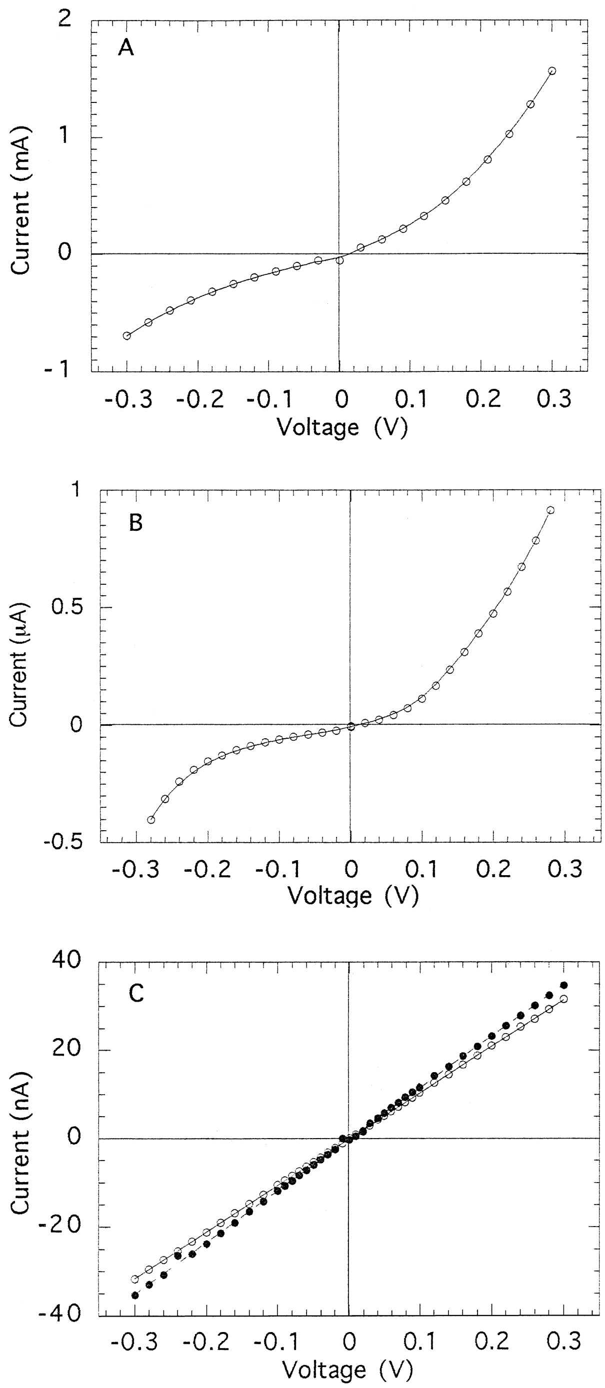

Fig. 1. I-V curve characteristics of CuBr thin-films in air at room temperature: (A). (Au/CuBr/Au) structure; (B). (Au/CuBr/Cu) structure; (C). (Cu/CuBr/Cu) structure, ● air, ○ ammonia.

We assume in the following that interfacial resistances are absent. The total conductivity of the CuBr thin films can in principle be calculated from characteristic (C) using the equation:

$$\sigma_{\text{tot}} = 1/(\lambda w R) \qquad (1)$$

Here, R is the measured resistance, 1 the distance between the grid lines, λ the total length of grid lines and w the thickness of the films. Using the experimental values, we obtain a total conductivity: $\sigma_{\text{tot}} \approx 5\ 10^{-7}$ S/cm, somewhat higher than the total conductivity of polycrystalline samples.[1,2]

The non-ohmic characteristics, observed with one or two gold electrodes, can be understood by blocking of the ionic current. According to Wagner's theory,[9] the observed exponential increase of current with applied potential is characteristic of a p-type semiconductor. This is consistent with our previous results on polycrystalline CuBr.[3–5] The partial conductivity of electron holes σ_h can be calculated from the simplified equation:[9]

$$\ln \mathrm{I} = \ln[\sigma_h RTS/(Fw)) + VF/RT \qquad (2)$$

Here, S is the electrode area and w the thickness of the film, T is the absolute temperature and F and R are Faraday's constant and the gas constant, respectively. In Figs 1(A) and (B), one notices immediately a large difference of the measured currents depending on whether one or two gold electrodes are used. Consequently, a hole conductivity of 10^{-5} S/cm is obtained with a Au/CuBr/Au structure, but only 10^{-8} S/cm with Au/CuBr/Cu. Defect chemistry provides a consistent interpretation of these results:CuBr is a copper-deficient compound with copper vacancies as majority ionic defect.[1–5] The ionisation of copper vacancies gives electron holes:

$$V_{Cu} \rightarrow V_{Cu}' + h^{\cdot} \qquad (3)$$

If the compound is in equilibrium with metallic copper, the copper deficiency takes the smallest possible value. Excess copper vacancies and electron holes are consumed.

$$Cu + V_{Cu}' + h^{\cdot} \rightarrow Cu_{Cu} \qquad (4)$$

According to this defect reaction, the hole conductivity, which is proportional to the hole concentration, decreases when we equilibrate CuBr

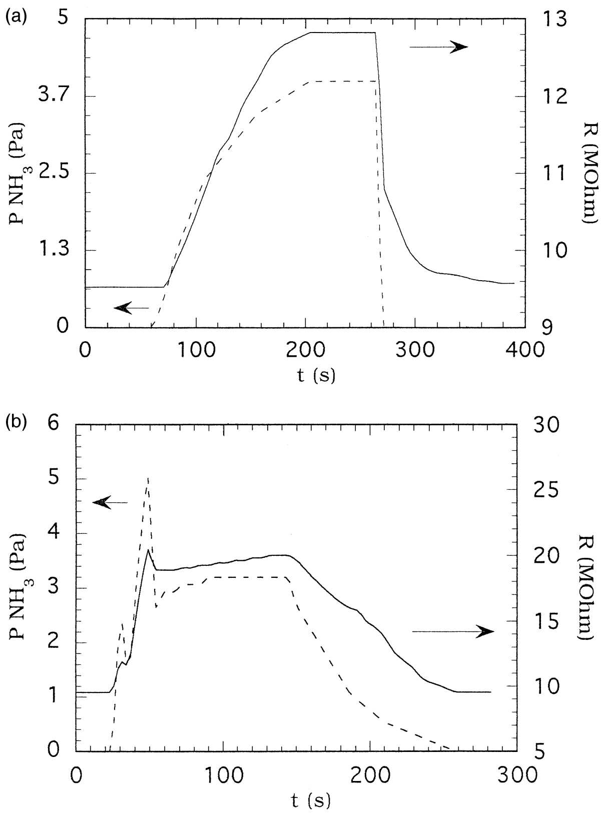

Fig. 2. Electrical response of CuBr thin-films in presence of ammonia: dotted line: pressure signal; full line: film resistance.

with copper metal. Altogether, these experiments confirm the importance of the choice of an appropriate contact metal. In the following experiments, we use reversible copper electrodes to monitor a change of the gas phase composition.

3.2 Effect of gaseous ammonia NH_3

Typical ambient temperature transients of the resistance of CuBr thin-films, due to introduction of ammonia gas, are shown in Fig. 2. One notices a nearly instantaneous response to the presence of ammonia and a fast resistance relaxation when the ammonia signal disappears. The corresponding time constant, calculated assuming an exponential dependence, is only a few seconds, which is a very encouraging result. Introduction of air or argon had no influence on the film resistance.

The I–V characteristics in presence of ammonia show a linear, ohmic dependence with a slightly decreased conductivity [Fig. 1(C), open dots]. Previous studies on silver halide thin-films[10–12] showed a similar decrease of conductivity. The adsorption of ammonia on the porous films has complex consequences for the film resistance : on the one hand, a conductivity increase is expected near the film surface due to space charge layer formation with increased metal vacancy concentration, but, on the other hand, adsorbed NH_3 molecules at intergranular boundaries increase the transfer resistances. The latter effect is more important and leads to an overall decrease of conductivity.[10–12] The CuBr thin-films present also a porous, granular microstructure and similar adsorption effects can be expected. It is impossible to separate space charge enhancement and blocking grain boundary effects with d.c. measurements, but impedance spectroscopy should be capable of discriminating between the different contributions.

Experiments at higher ammonia pressure ($p >$ 20 Pa) showed polarization effects which are currently not understood, but may be due to a saturation with NH_3 molecules. Possible ageing effects of the thin-films and their influence on the sensor characteristics are currently investigated after in-situ heat treatments.

4 Conclusion

Our experiments confirm the importance of an appropriate electrode metal for measuring d.c. characteristics: major differences are observed using reversible copper and blocking gold contacts. A very fast electrical response is noticed on modification of the ammonia partial pressure in the gas atmosphere. Subsequent work will be focused on the major issues selectivity, saturation and long-time stability of the sensors.

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