RTEP2014 IOP Publishing
IOP Conf. Series: Materials Science and Engineering **81** (2015) 012088 doi:10.1088/1757-899X/81/1/012088

Application of secondary ion mass spectrometer for measuring the diffusion profiles in alkali-halide crystals

A V Chernyavskii[1] and M S Kaz[2]

[1] National Research Tomsk Polytechnic University, Tomsk, Russia

[2] National Research Tomsk State University, Tomsk, Russia

E-mail: chernyavski@tpu.ru

Abstract. Depth profiles of magnesium, fluorine and oxygen impurities was examined in the surface layers of alkali-halide KBr crystals using method of secondary ion mass spectrometry. Samples of potassium bromide, coated with a surface film of magnesium fluoride were subjected to isothermal diffusion annealing in air at various times. It is shown that the diffusion of O ions occurs from the ambient atmosphere besides the diffusion of Mg and F ions during annealing of KBr crystals. Accurate estimation of the diffusion coefficients of cationic impurity Mg requires taking into account the possible interaction of this impurity and oxygen.

1. Introduction

A significant number of solid phase reactions, which determines the real defect structure and the most important physical, chemical properties of inorganic materials, are among the diffusion-controlled. Radiation impact is one of the most promising methods and greatly accelerates the process of sintering of powders of alkali salts [1], a number of oxides [2], as well as intensifies the process of synthesis of complex oxide compounds [3, 4]. Opportunity to stimulate the diffusion phenomena in ionic dielectrics by flows of ionizing radiation, especially in the most practical interest region of high temperatures, is an actual problem. Therefore, we carried out experiments using electron beams, providing heating of the samples and the high level of excitation of the electron and nuclear subsystems of crystals, as well as radiation defect, for the study of their effect on the diffusion mass transfer model in alkali halide crystals, the results of which are given in [5-7].

Secondary-ion mass spectrometer MS7201M (PC "Electron", USSR) was used in these studies to measure the diffusion profiles. The design features of the instrument required to implement additional steps for sample preparation and measurement. More detailed methodology of research on this device is described in our previous works [5, 8]. In addition, analysis of the results of studies high temperature diffusion of Mg impurities from a variety of chemical compounds (MgF_2, Mg) in ionic crystals LiF [9] and KBr [8] showed that the calculated value of the diffusion coefficient has always been less for investigated impurities than the known values of bulk diffusion coefficients [10] and this difference was (2-3) an order of magnitude. The original chemical state of impurity cations had no significant effect on their diffusion characteristics in this works.

It has been suggested that an impurity film reacts with oxygen to form metal oxide under annealing in contact with the air. A similar problem faced by the authors of [11] in the study of the diffusion of cobalt impurity in potassium chloride, for which extremely low diffusion coefficients were also received. To substantiate this hypothesis, we studied high-temperature diffusion of Mg, F, O impurities in the surface layers of ionic crystals KBr during thermal annealing, the results of which are given in this article.

2. Material and experimental methods

Secondary-ion mass spectrometer PHI 6300 (Perkin-Elmer PHI 6300 Ion Microprobe, USA) was used to measure the depth profiles in this work. The instrument allows analysis of both positive and negative secondary ions. Thus, it is possible to conduct a study of depth profiles of cationic and anionic impurities in ionic crystals. Study of the profiles of anionic impurities could not be done by using a mass spectrometer MS7201M as the device allows analysis only the positive secondary ions. The yield of secondary positive ions is very small for the investigated anionic impurities in KBr crystals. Primary source of Cs^+ ions with energy of 7 keV was used for etching samples in PHI-6300. The sample surface is scanned by beam of focused primary ion with sides of the scan area of 500 μm. To neutralize the positive charge building up on the surface of the sample during analysis, electron gun was used, the electron beam of which is scanned sample surface. After the measurements it was determined the depth of the etching crater using the profilometer, and then there were built dependencies of the intensity of the secondary ion impurities signal from the depth. Secondary positive ions were analysed for magnesium impurities and negative ions - for oxygen and fluorine impurities. In our experimental conditions, we can assume that the signal intensity of the secondary ions is directly proportional to the concentration of the elements of interest in the sample.

Single crystals of potassium bromide were used in our experiments. Magnesium fluoride film with about 400 nm thickness was deposited by thermal evaporation in vacuum on the surface of the samples. Unlike the previously used technique [8], the film was deposited on the entire surface of the sample. Then, the film sample surface was superimposed another crystal, and they are pressed together. Thereafter, the samples were subjected to isothermal annealing in air at 650°C in an electric resistance furnace. Annealing times were 30, 90 and 600 min.

3. Experimental results and discussion

Figure 1 shows the depth profiles of the magnesium impurity ions in the crystals of potassium bromide, subjected to annealing with different duration, and depth profile of magnesium ions in the original sample before the diffusion annealing. Dependencies the signal intensity of the secondary ions of magnesium on the depth presented in relative units. Signal intensity was normalized to the intensity value at the boundary surface, the impurity film - crystal.

As can be seen from figure 1 the depth of penetration and the number of embedded impurities increases with increasing time of annealing, indicating a diffusive mass transfer of impurities in the depth of the crystal. However, the calculated value of the diffusion coefficient for magnesium impurities for these measurements is equal 3×10^{-12} cm^2/s and comparable to values previously obtained for the diffusion of impurity from the metal films [8]. Diffusion of magnesium ions previously nobody investigated in KBr crystals. In the literature [10], there are experimental data relating to the divalent cationic impurities other varieties. Typical values for their diffusion coefficients corresponding to temperature of our experiments are in the range of 10^{-8}–10^{-10} cm^2/s. The calculated value of the diffusion coefficient, determined by us for magnesium ions in potassium bromide, was considerably reduced by orders of magnitude. This result confirmed our earlier results [9].

To numerically evaluate the diffusion coefficients of magnesium ions approximation of the experimental profiles was carried out by solution of Fick's equation for the diffusion from the region with a constant concentration in a semi-infinite crystal. However, such evaluation gives approximate results, as seen in this model only diffusion of one impurity is considered and does not account diffusion of other ions, as well as their possible interactions between them. In our experimental conditions diffusion of oxygen ions and fluoride was also observed that can be seen from these results further.

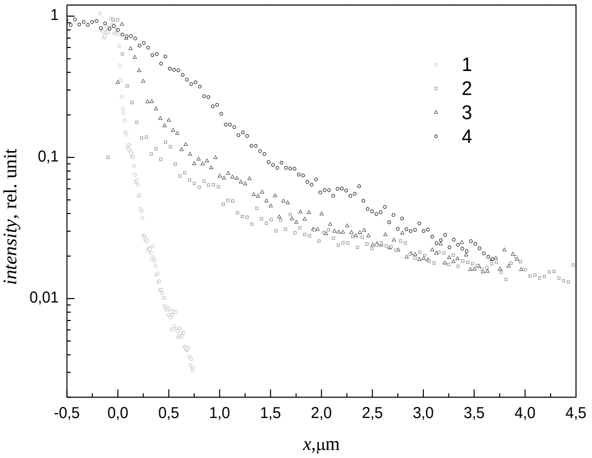

Figure 1. Magnesium depth profiles in the original sample without annealing (1) and samples annealed for various duration (2 - 30 min., 3 - 90 min., 4 - 600 min.) at 650°C

Figure 2 shows the depth profiles of F and O ions for the initial sample and the sample after annealing at 650°C for 600 min. Signal intensity of the secondary ions of oxygen (in the graph shown in absolute units) increases by an order of magnitude or more for a sample subjected to an annealing, as compared to the initial sample. Moreover, the oxygen penetrates into the MgF_2 film, which is on the sample surface and the potassium bromide crystal itself.

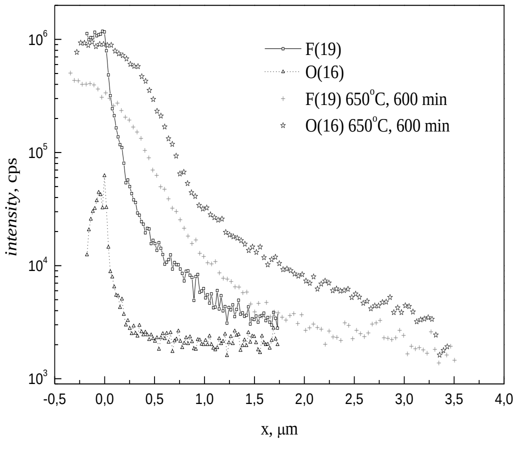

Figure 2. Depth profiles of oxygen and fluorine ions in the original and annealed samples

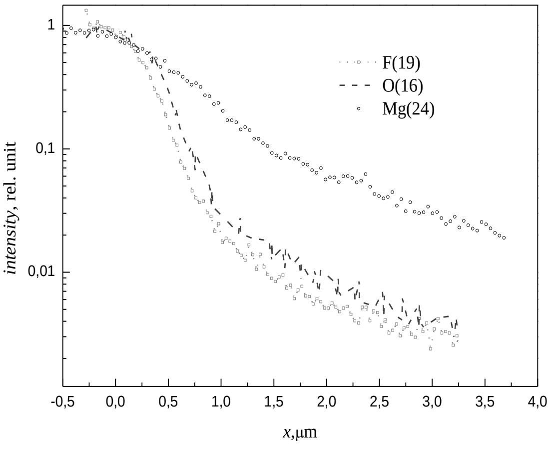

Figure 3. Depth profiles of O, F, Mg impurities in KBr crystal followed by 600 min. annealing at 650°C

The depth of penetration of impurity ions of fluorine and oxygen was essentially less compared to the depth of penetration of magnesium ions, as best seen in figure 3 (secondary ion intensity signal is given in relative units), which shows the depth profiles of indicated ions. This indicates a lower activity of the diffusion fluorine ions and oxygen ions in comparison with magnesium.

The results obtained confirm that the diffusion of atmospheric oxygen simultaneously takes place in the sample and source diffusing film in the diffusion of magnesium in KBr crystal from MgF_2 film.

In the crystal lattice of the oxygen can react with the cation impurity to form an oxide molecule. Oxide molecules in the investigated temperature range are quite stable. We can assume that because of this impurity cation penetrates into the surface layers in a bound state as inactive oxide molecular complexes. Thus, for the numerical determination of the diffusion coefficients of impurities in these experiments, it is necessary to take into account the fact of simultaneous penetration of magnesium, fluorine, oxygen impurities in the crystals as well as the information on the form of penetration of impurities in the crystals and therefore, the development of a specific diffusion model for the solution of the Fick equation are required.

4. Conclusions

According to the presented results following conclusions can be:
- oxygen diffusion occurs from the ambient atmosphere during annealing on air for samples of the alkali halide crystals with deposited on their surface of the metal halide film as a source of impurity for diffusion experiments;
- correct estimation of diffusion coefficients of cation impurities requires to consider the possible interaction of these impurities with oxygen in ionic crystals.

Acknowledgements

This work was supported by the Ministry of Education and Science of the Russian Federation within the framework of the government “Science” program.

References

[1] Yu M Annenkov, T S Frangul’yan and A V Voznyak 1991 *Soviet powder metallurgy and metal ceramics* **30(8)** pp 634–636
[2] V V Grishaev, A P Erastova, B M Lebed', Yu G Saksonovand G Ya Fedorova 1988 *Izv. Akad. Nauk SSSR. Neorg. Mater.* **24(11)** pp 1857–60
[3] V L Auslender, I G Bochkarev, V V Boldyrev, N Z Lyakhov and A P Voronin 1997 *Solid State Ionics* **101-103**(PART 1) pp 489-493
[4] V V Boldyrev, A P Voronin, O S Gribkov, E V Tkachenko, G R Karagedov, B I Yakobson and V L Auslender 1989 *Solid State Ionics* **36(1-2)** pp 1-6
[5] A P Surzhikov, A M Pritulov, S A Ghyngazov and A.V Chernyavskii 2000 *Perspekt. Mater.* **1** pp 30-34
[6] A P Surzikov, T S Frangulyan and A V Chernyavskii 2001 *Perspekt. Mater.* **3** pp 24-29
[7] A P Surzhikov, T S Frangulyan, S A Ghyngazov and A V Chernyavskii 2004 *Perspekt. Mater.* **2** pp 77–82
[8] S A Gyngazov, A P Surzhikov, T S Frangul'yan and A V Chernyavskii 2002 *Russian Physics Journal* **8** pp 753-758
[9] A P Surzhikov, A V Chernyavskii, S A Ghyngazov and T S Frangulyan 2002 *Russian Physics Journal* **12** pp 1190-94
[10] F Beniere 1972 Diffusion in ionic crystals *Physics of Electrolyte*s vol 1 ed J Hladik (London-New York:Academic Press) chapter 6
[11] D Damien and K V Reddy 1983 *Indian J. Pure Appl. Phys.* **21(3)** pp 133–136