

STRUCTURE AND FORMATION OF FILMS OF ZIRCONIA-BASED SOLID ELECTROLYTE

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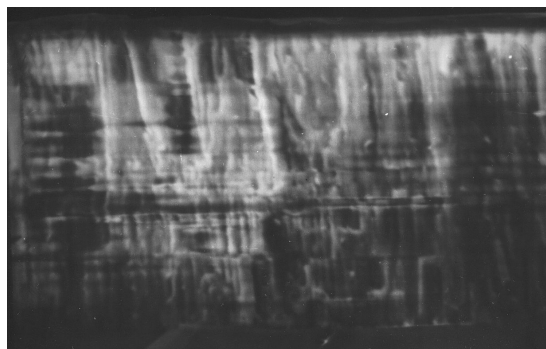
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Introduction

The structure and the formation of films of a zirconia-based solid electrolyte, which were prepared by ion plasma sputtering, were studied using scanning and transmission electron microscopy methods.

Results and discussion

The structure of films of zirconia-based solid electrolytes was analyzed in a scanning electron microscope. It was found that both one- and multilayer films (Fig. 1,2) of zirconia, which was stabilized to its cubic modification, up to 10 μm thick had a columnar structure, that is, consisted of mutually adjoining crystallites, which generally were oriented perpendicularly to the film surface. The observed deviation of the crystallites from the normal direction to the film plane was not over 15° and was explained by the mutual misorientation of the target and the substrate.

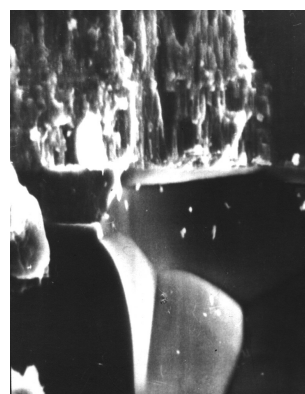


x 5000

Fig. 1. Electron microscopic image of a fracture of a monolayer film of the zirconia-based solid electrolyte

A significant property of the multilayer films, namely a structural "independence" of adjacent layers, was revealed. This property showed up as an offset of structural elements and grain boundaries between layers. Therefore, it was possible to control structure-sensitive parameters of the solid-electrolyte films.

Considering the obtained experimental data, it is possible to propose a model of the formation of a porous structure of the films of zirconia-based solid electrolytes. The model assumes the formation of pores and submicropores when vacancies, which are trapped during sputtering of the solid-electrolyte films (the sputtering temperature was $T_f < 0,3T_{\text{melt}}$), pass to sinks and then condense [1]. The sinks are boundaries between the crystallites forming the film structure.



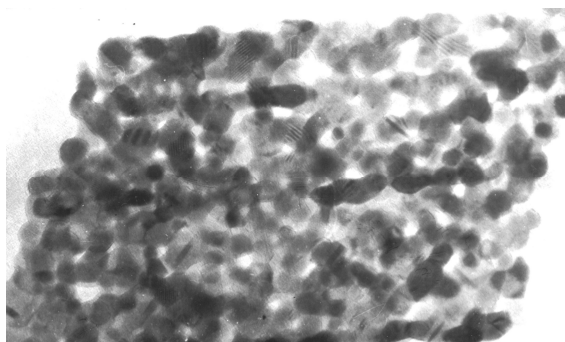
x 5000

Fig. 2. Electron microscopic image of a fracture of a multilayer film of the zirconia-based solid electrolyte

The transmission electron microscopy was used to study the initial stage of the formation of the films of zirconia-based solid

electrolytes, which were prepared by ion plasma sputtering on a glass-ceramic substrate having a thin (~10 nm) layer of amorphous carbon.

It was found that at the initial stage of its formation the film of the zirconia-based solid electrolyte consisted of nanocrystallites arranged randomly or in some order. The nanocrystallites had an irregular round shape and were ~40 nm in size on the average. Ordered nanocrystallites generally formed squares, but sometimes they were shaped as parallelograms (Fig. 3). The nanocrystallites had a kind of self-organization.



x 200000

Fig. 3. An ordered nanocrystalline structure of a film of the zirconia-based solid electrolyte in the form of a parallelogram

An electron diffraction study of the ordered nanocrystalline entities demonstrated that the electron patterns were similar to those of block crystals. As distinct from the block crystals, the ordered nanocrystalline entities had discontinuities (Fig. 3). The electron patterns of the ordered nanocrystalline entities suggested a high orientation coordination of their constituent nanocrystallites (Fig. 4)

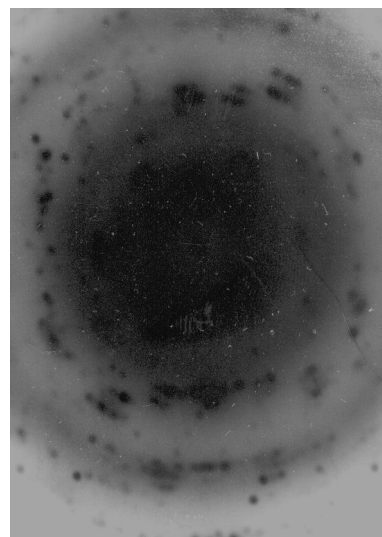


Fig. 4. The electron diffraction pattern of the ordered nanocrystalline entity

Since the nanocrystallites were separated from the substrate with a layer of amorphous carbon, one might think that the ordered arrangement of the nanocrystallites was due to an auto-orientation mechanism, which operated at all stages of the growth of the ordered nanocrystalline forms of the films of the zirconia-based solid electrolyte.

Conclusion

The simultaneous analysis of the results of the study into the structure and the formation of the solid-electrolyte films led to the following conclusion: the nanocrystalline structure of the solid-electrolyte films at the initial stage of their formation caused the appearance of a columnar structure of the films of the zirconia-based solid electrolyte during their sputtering.

References

- [1] Palatnik L.S., Fuks M.Ya., Kosevich V.M. The Mechanism of Formation and the Substructure of Condensed Films. Moscow, Nauka, 1972, 320 p.