PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 18, № 2 (2017) P. 184-186
***DOI: 10.15330/pcss.18.2.184-186***

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 18, № 2 (2017) С. 184-186

UDK 539.23+539.234

ISSN 1729-4428

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# The Changes of Structure and Electrical Properties of Thin Films During Long-Term Aging

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The changes of surface structure and electrical properties of crystalline thin films of ternary compounds (La, Y, Sc)-(Ni, Fe)-Ge with metal content not more than 50 at. percent, which are obtained by vacuum deposition, are investigated. The directions of growth defects of films in aging over 20 years shown also as the influence of aging on the electrical properties of the condensates are analyzed.

**Key words:** thin films, aging, electron microscopy.

*Article acted received 19.03.2017; accepted for publication 05.06.2017.*

## Introduction

Obtaining of crystalline thin-film structures of ternary compounds is a difficult technological challenge, which is sold only under certain technological requirements taking into consideration thermodynamic conditions of deposition. Most such crystalline thin-film materials received at high deposition rate ($v_p > 10^3$ nm/s) by latest methods of vacuum condensation (plasma technology, a method of electrical explosion) or with the help of special technical applications by some methods of thermal evaporation materials (discrete evaporation of compound, coordinated evaporation from two independent sources, etc.) when $v_p < 30$ nm/s. Structure and properties time stabilization of materials depend on their composition, technological parameters of deposition process and conditions of exploitation [1, 2]. In this case most of investigators noted, that the physical characteristics of thin film materials, obtained from thermal evaporation, more correspond to massive sample, but are less stable in structure and properties, compared with samples obtained at high deposition rate.

The aim of this work was to study temporal changes in the structure and conductive characteristics of ternary compounds 25 at% RE (rare earth: La, Y, Sc)-25 at% - Me (transition metals: Ni, Fe)-50 at% Ge crystalline condensates, most of which have been identified as compound of stoichiometric phase REMeGe2, and thin films of binary germanides ScGe2 (67 at% Ge).

## I. Experimental

The crystalline thin films that have been preserved during long-term aging (along 20 years) in storage conditions or have been regularly exploited as elements of thermoelectric sensors (samples with scandium) are materials for research. All samples were produced by thermal vacuum deposition (samples with lanthanum and scandium – by discrete evaporation alloys, with yttrium – by coevaporation of components) on the glass ceramic substrates in a vacuum of $10^{-3}$ Pa. The deposition rate $v_p$ was varied from 4 to 30 nm per sec. Film thickness $\boldsymbol{h}$ = 60 – 120 nm was controlled using the microinterferometer. The electron microscopy investigations were carried out using scanning microscope EVO 40XVP.

## II. Results and discussion

Long-term aging has led to an increase in electrical resistance of crystalline condensates. The deviations from the initial value depended from the conditions of condensation (mainly in such indexes as substrate temperature during deposition $T_n$, thermodynamic saturation $Z_p$, the deposition rate $v_p$, etc.), type of material (compounds), conditions of storage or exploitation. The slightest deviation from the initial electrical resistance at the long aging characterized by crystalline condensates $Y_{25}Fe_{25}Ge_{50}$, obtained by

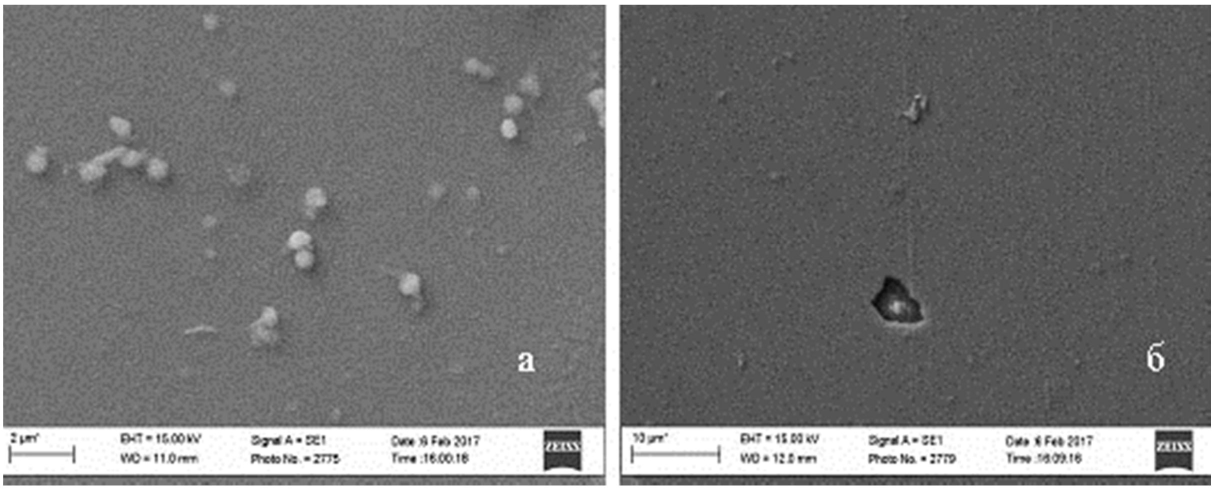


**Fig. 1.** Morphology of $Y_{25}Fe_{25}Ge_{50}$ thin films, obtained by $v_p$ = 6 nm/sec and $T_p$ = 710 K by coevaporation, after long aging in desiccator (a - X6000; b - X2000; the scale in the left corner micrographs is shown).

coevaporation on a substrate at $T_p$ = 710 K at a rate $v_p$ = 6 nm per sec, and $LaNiGe_2$, which were obtained under the same conditions. For the first sample deviation was 15 – 25 %, for the second – 26 - 40 %. The thin film crystalline samples of ternary compounds of Sc and La, which were obtained at $T_p$ = 650 K, characterized by significant deviations of electrical resistance – up to 80%. However, the most unstable were found crystalline $ScGe_2$ thin films, which initially during long time (4 years) exploited as thermocouple element. It has a deviation 3 times from the nominal value of electrical resistance (the departure from the permissible value of thermopower observed on 3-year exploitation).

The crystalline films of ternary compounds RE-Me-Ge obtained at substrate temperature more than 580 - 600 K. Minimum substrate temperature at which condensate has completely crystalline structure depends on thermodynamic condition of evaporation, deposition rate $v_p$, value of vacuum, type of substrate, film thickness. The best temporal stability of electrical characteristics were obtained on thin film which condensated at high maximum substrate temperature allowable for the glass ceramic substrates. The structure of the surface of such films after long decades of aging uniformly smooth, with no visible defects such as pores and cavities (Fig. 1, a). However, the growth of crystal conglomerates predominantly round shape with dimensions $0.5 \cdot 10^{-6}$ m observed. The defects of thin films which had the form of pores were identified as flaws of initially receiving during condensation, which, however, not grew at a long time aging (Fig. 1, b).

Similar stable characteristics showed crystalline condensates of ternary compound $LaNiGe_2$, which, at the time, were obtained in the same conditions as the previous films. The surface structure of such thin films is pure, without large defects, but traces of recrystallization and new formation of structures whose size could reach up to $1{,}6 \cdot 10^{-5}$ m in some places observed (Fig. 2).

Lowering the temperature of the substrate, increasing deposition rate, thermodynamic saturation during condensation, changes of the type of substrate, also other deviations necessarily lead to transformations in the long-term stability structure and properties of condensates [3-5]. Such materials have peculiar to recrystallization and reduced adhesion to the substrate. Basically, these areas occur in places of microscopic defects and roughness of the substrate. The characteristic microscopic cracks and grooves with width $d = 3 \cdot 10^{-6}$ m, formed by recrystallization and cracking of the material, are typical for thin films obtained by $T_p$ = 670 K on the glass ceramic substrates. Crystal tumors that grow from condensation, can have needle end, which is typical of long aging process. In fact, the increasing of value of defects leads to a significant increase in electrical resistance (Fig. 3).

However, the most unstable structure and, therefore, the physical properties found in crystalline $ScGe_2$ films, recrystallization processes in which extremely active at the 4-5 years aging (Fig. 4). This material was exploited as a thermocouple element in a narrow 273 – 393 K temperature range of measuring. But so slight thermal cycling revealed all the negative points that have arisen during obtaining condensate.

After all, the probability to find the nucleuses that oriented in different directions for tens of arcseconds in

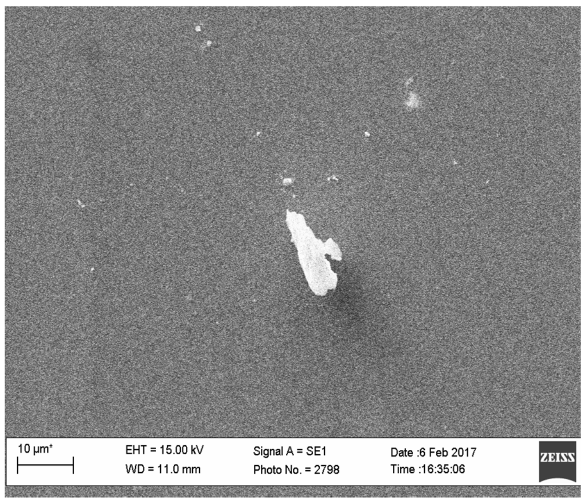


**Fig. 2.** Electron micrograph of crystalline $LaNiGe_2$ thin films, obtained by discrete evaporation at $v_p$ = 5 nm/sec and $T_p$ = 700 K, after 20 years of aging (X1000).

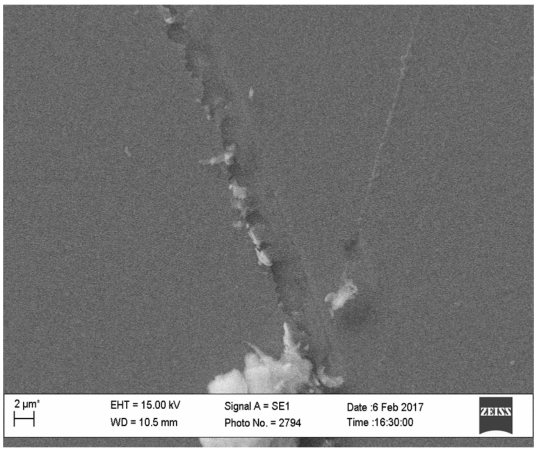


**Fig. 3.** The repercussion of recrystallization processes during the long aging in crystalline $LaFeGe_2$ condensate (X2000).

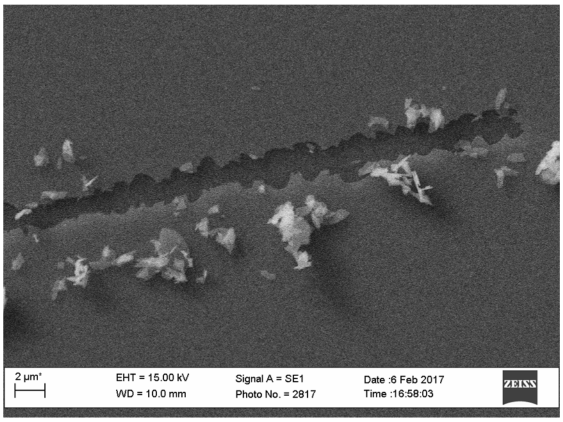


**Fig. 4.** Specifics of the structure of the crystalline $ScGe_2$ thin film after long aging (X3000).

condensate, which obtained with small thermodynamic saturation, is very large. Such disorientation is sufficient for the formation of dislocations, defects, stacking faults or areas of great value stress concentration. They all are evident in long-term aging by intensifying destabilizing process, which have place between substrate and thin film.

## Conclusion

The research has found that the substrate temperature is an important parameter, which not only initially set passage of crystallization process and the impact on condensate structure, but also course of the aging process condensate. This shows the dominant contribution of degradation processes in the structure, diffusion material and drain defects during aging. The significant difference in the changes in the structure of thin film materials that have been in exploitation indicates such possible influence as environment (as water vapor) on the condensate and preserving the strength of adhesive bonds during the thermal cycling.

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# Зміна структури та електропровідних характеристик тонких плівок під час довготривалого старіння

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Досліджено зміну структури поверхні та електропровідні характеристики кристалічних тонких плівок тернарних сполук (La, Y, Sc)-(Ni, Fe)-Ge з вмістом металу не більше 50 ат. %, які були отримані методами вакуумного напилення. Показано напрямки росту дефектності плівок при старінні більше 20 років, проаналізовано їх вплив на електропровідні характеристики конденсатів.

**Ключові слова:** тонкі плівки, старіння, електронна мікроскопія.