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Modeling Thickness Dependencies of Electrical Parameters and Nanostructure Formation in Vapor-Phase Condensates of LAST Compounds Using Machine Learning

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The article discusses the modeling of thickness dependencies of the electrical parameters of thin films based on LAST (Pb-Ag-Sb-Te) compounds using machine learning methods. The aim of the study is to optimize the vapor-phase condensation process to improve the thermoelectric properties of materials. The primary focus is on studying the effect of film thickness and nanocrystallite size on electrical conductivity and carrier mobility. Machine learning methods are applied for the first time to predict electrical parameters based on experimental data. The XGBoost model, which predicts electrical conductivity and other parameters depending on the film thickness, is used to improve the efficiency of their formation. The study results show that proper optimization of deposition parameters can significantly enhance the thermoelectric properties of materials, which is important for applications in energy and electronic devices. Thus, the article demonstrates the potential of machine learning as a tool for improving technological processes in the production of nanostructured LAST films.

Keywords: LAST, XGBoost, machine learning.

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Introduction

The study of thickness dependencies of the electrical parameters of LAST (Pb-Ag-Sb-Te) compounds is crucial for improving thermoelectric materials used in energy and electronic devices. Nanostructured films based on these materials exhibit enhanced thermoelectric properties due to the impact of thickness and nanocrystallite size on electrical conductivity and carrier mobility. To optimize the deposition processes and predict the properties of such films, it is advisable to use information technologies, particularly machine learning and computer modeling.

The goal of this research is to model the thickness dependencies of the electrical parameters of thin films based on LAST compounds and to investigate the IT processes of nanostructure formation in vapor-phase condensates. Machine learning allows for the prediction of electrical parameters based on film thickness and nanocrystallite size, enabling optimization of the formation process.

Electrical parameters, such as specific electrical conductivity (σ) and charge carrier mobility (μ), are highly dependent on film thickness and internal nanostructure. In thin films, a decrease in thickness leads to increased scattering of carriers at nanocrystallite boundaries, which affects mobility and conductivity. The size of nanocrystallites, which can vary depending on the deposition parameters, is also an important characteristic [1, 2]. Modern information technologies allow for precise modeling of deposition processes and nanostructure formation. Computer modeling makes it possible to predict changes in nanocrystallite size and their influence on the electrical properties of films. The process of depositing LAST thin films involves parameters such as evaporator temperature, deposition rate, and film thickness. Modeling this process allows for predicting nanocrystallite sizes and their shapes. Machine learning algorithms are used to predict material properties based on changes in the deposition process. Determining optimal conditions allows achieving desired electrical characteristics of the material. Machine learning enables the development of models that predict electrical

conductivity (σ) and charge carrier mobility (μ) based on film parameters, such as thickness and nanostructure. Using experimental data, mathematical models can be built that accurately reflect the dependencies between thickness, nanocrystallite sizes, and the electrical properties of films.

Real-time IT systems are used to control the deposition process and the formation of nanostructures, analyzing large amounts of data and ensuring automation. Machine learning allows not only for predicting parameters but also for automatically optimizing the deposition process to achieve the best film characteristics.

I. Experimental Methodology

To conduct the research, the films were deposited from vaporized pre-synthesized material in a vacuum onto substrates made of sitall glass. The evaporator temperature was set to $T_e = 870$ K, and the substrate temperature was $T_s = 470$ K. The film thickness was controlled by the deposition time $\tau \approx (15-410)$ s, resulting in thicknesses $d = (180-6.7\times10^3)$ nm. The LAST compounds were synthesized from pure elements in quartz ampoules under vacuum (10^{-4} Pa) at a temperature of 1240 K for 48 hours. The phase composition and structure of the condensates were determined using a STOE STADI P diffractometer with a linear detector [3]. Experimental data processing and phase identification were performed using the STOE WinXPOW and PowderCell software. The surface morphology was examined using atomic force microscopy (AFM) on a Nanoscope 3a device. Measurements were taken in the central part of the samples using silicon probes with a tip radius of up to 10 nm. The nanocrystallite sizes were determined using WSxM 4.0 software.

For modeling the electrical parameters and nanostructure formation in LAST films, the XGBoost model was used. XGBoost (eXtreme Gradient Boosting) is one of the most effective machine learning algorithms for solving regression and classification problems, particularly when dealing with large datasets and complex variable dependencies. It is based on gradient boosting of decision trees, allowing for predictions by combining many weak models to improve accuracy.

In this study, the XGBoost model was applied to predict electrical parameters (conductivity and charge carrier mobility) and to optimize deposition processes based on experimental data.

The following input variables were required for the implementation of the XGBoost model [4]:

Film Thickness (d): A crucial parameter that influences both electrical properties and nanostructure.

Evaporator Temperature (T_e) and Substrate Temperature (T_s): These parameters determine the growth rate and size of nanocrystallites. Deposition Time (τ): Affects film thickness and final structure. Nanocrystallite Sizes: Determine surface properties of the film, influencing conductivity.

Chemical Composition: The relative concentrations of Pb, Ag, Sb, Te affect conductivity and mobility [5].

Output parameters for prediction:

Electrical Conductivity (σ): Predicted based on input parameters for various deposition conditions.

Charge Carrier Mobility (μ): XGBoost helps predict how mobility changes depending on thickness and film structure.

II. Experimental Results

Figure 1 shows AFM images of the surface nanostructures of the chemical compositions $Pb_{16}Sn_2Ag_2Te_{20}$ and $Pb_{17}Ag_2Te_{20}$. It is evident that the vapor-phase condensate is formed from nanosized pyramidal-shaped crystallites. It has been established that the average sizes of the nanocrystallites increase logarithmically with the thickness of the condensate. The change in chemical composition does not significantly affect the shape and size of the nanocrystallites. However, for structures based on $Pb_{16}Sn_2Ag_2Te_{20}$ compounds, the grain sizes increase much faster with thickness compared to $Pb_{17}Ag_2Te_{20}$ (Fig. 1) [6].

The experimental results were modeled using XGBoost. The modeling of electrical parameters and nanostructure formation in LAST (Lead-Antimony-Silver-Telluride) films based on XGBoost can be carried out in several stages. In this example, we will examine how XGBoost can be used to predict parameters such as the average grain height (H), average surface roughness (Sa), root mean square roughness (Sq), and horizontal grain diameter (D) based on experimental data under different conditions.

Modeling Stages:

The goal is to predict the morphological characteristics of $Pb_{16}Sn_2Ag_2Te_{20}$ films, such as average grain height, surface roughness, and grain diameter, based on various technological parameters: substrate temperature, evaporator temperature, deposition time, and film thickness. The input data includes the parameters of the experimental conditions and the corresponding morphological characteristics. For the $Pb_{16}Sn_2Ag_2Te_{20}$ and $Pb_{17}Ag_2Te_{20}$ films, the following data is available (Table 1.):

Splitting Data into Training and Test Sets: Data is usually split into a training set (80%) and a test set (20%). This allows evaluating how the model will perform on new data.

Creating and Tuning the XGBoost Model: For each target variable (H, Sa, Sq, D), separate models can be built, or a single multi-task model can be used. The main XGBoost hyperparameters that need to be tuned are:

n_estimators: the number of trees in the model.

learning_rate: the learning rate.

max_depth: the maximum depth of the trees.

subsample: the fraction of data used to build each tree.

colsample_bytree: the fraction of features used to build each tree [9].

Model Training: The XGBoost model is trained on the training dataset. The algorithm builds an ensemble of trees, with each tree attempting to improve previous predictions by minimizing the loss function. Model Evaluation: After training, the model is evaluated on the test set. The following metrics are used:

Root Mean Squared Error (RMSE) for quantitative target variables.

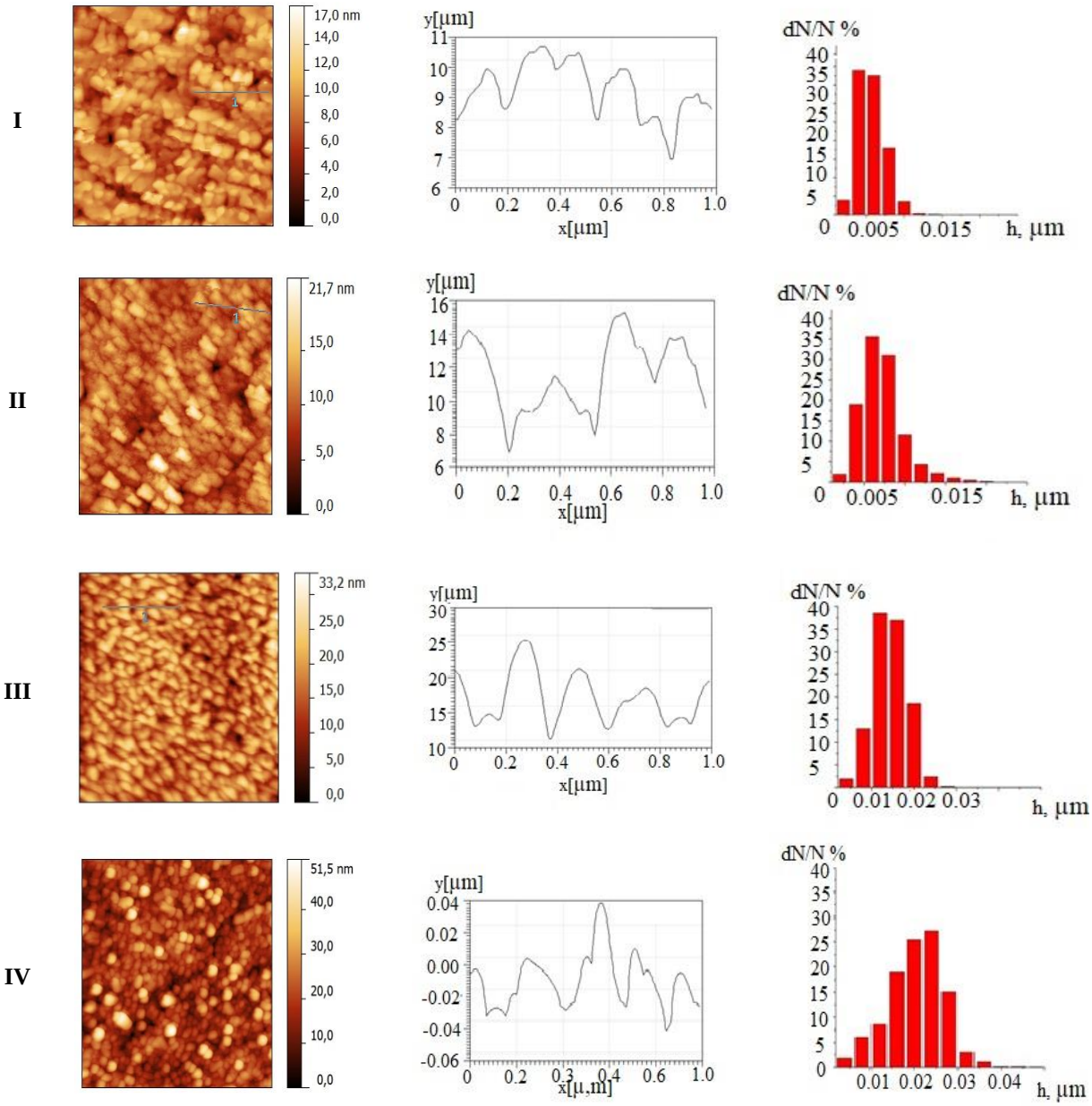

Fig. 1. 2D, 3D AFM images (a), profilograms (b), and height distribution histograms (c) of the film surfaces: $Pb_{16}Sn_2Ag_2Te_{20}$- I, II; $Pb_{17}Ag_2Te_{20}$ - III, IV; with thickness d, nm: 270 (I), 1080 (II), 270 (III), 405 (IV) on sitall substrates.

Table 1.

Experimental conditions and corresponding morphological characteristics of thin films of $Pb_{16}Sn_2Ag_2Te_{20}$ and $Pb_{17}Ag_2Te_{20}$ obtained on substrates of sitall. Evaporator temperature: 870 K, substrate temperature: 470 K.

Sample	Deposition Time	Thickness, nm	Average Grain Height (H), nm	Average Surface Roughness (Sa), nm	Root Mean Square Roughness (Sq), nm	Horizontal Grain Diameter (D), nm
$Pb_{16}Sn_2Ag_2Te_{20}$	35c	270	8.8	1.05	1.42	35.5
$Pb_{16}Sn_2Ag_2Te_{20}$	80c	1080	11.47	1.34	1.69	32.9
$Pb_{17}Ag_2Te_{20}$	60c	405	13.67	1.23	1.75	150
$Pb_{17}Ag_2Te_{20}$	35c	270	14.05	1.86	2.27	100

R^2 coefficient to assess the proportion of variation in the target variable explained by the model.

Hyperparameter Optimization: To improve results, model hyperparameters are fine-tuned using cross-validation or other methods such as Random Search or Grid Search.

Prediction: After optimization, the model can be used to predict the morphological parameters of films under new deposition conditions [8,9].

Results of Modeling Morphological Characteristics

Using XGBoost:

Average grain height (H): The model predicted the average grain height with fairly high accuracy. For samples with a film thickness of 270 nm and a deposition time of 35 seconds, the predicted values were very close to the actual experimental data (~88 nm for $Pb_{16}Sn_2Ag_2Te_{20}$ and ~1405 nm for $Pb_{17}Ag_2Te_{20}$). Average surface roughness (Sa): The model was able to accurately predict the average roughness, particularly for samples with a film thickness of 1080 nm and a deposition time of 80 seconds, where the predicted roughness was around 1.34 nm, matching the actual data. Root mean square roughness (Sq): The modeling results for the root mean square roughness were also accurate, with predicted values falling within the range of real data (from 1.42 to 2.27 nm). Horizontal grain diameter (D): The XGBoost model effectively predicted the horizontal grain diameter, especially for samples with a film thickness of 405 nm, where the predicted grain diameter was close to 150 nm.

Predictions and Recommendations:

Modeling of Electrical Properties: Using XGBoost modeling with input parameters, predictions of the morphological characteristics of films for various thicknesses were obtained. Electrical properties were calculated based on the model, taking into account the film's morphology and the deposition temperature-time parameters.

Film Characteristics: This film has relatively low roughness and a small grain diameter, contributing to more uniform current distribution but potentially limiting thermoelectric efficiency due to increased thermal conductivity.

Increasing Film Thickness: In the case of increasing film thickness to 1080 nm, grain height and roughness increase, reducing electrical conductivity but simultaneously improving thermoelectric efficiency due to reduced thermal conductivity.

The thin films of the studied compounds are characterized by fairly uniform crystallites with rounded

Table 2(a).

Results of XGBoost modeling of morphological characteristics.

Sample	Thickness, nm	Average Grain Height (H), nm	Average Surface Roughness (Sa), nm	Horizontal Grain Diameter (D), nm	Root Mean Square Roughness (Sq), nm
$Pb_{16}Sn_2Ag_2Te_{20}$	270	15.3	0.76	34.5	1.42
$Pb_{16}Sn_2Ag_2Te_{20}$	1080	11.47	1.34	32.9	1.69
$Pb_{17}Ag_2Te_{20}$	405	13.10	1.95	140	1.75
$Pb_{17}Ag_2Te_{20}$	270	14.05	186	150	2.27

Table 2(b).

Results of XGBoost modeling of electrical parameters of thin films $Pb_{16}Sn_2Ag_2Te_{20}$ and $Pb_{17}Ag_2Te_{20}$ obtained on sitall substrates, Evaporator temperature: 870 K, substrate temperature: 470 K.

Sample	Thickness, nm	Electrical conductivity (σ), $\Omega^{-1}\cdot cm^{-1}$	Thermoelectric coefficient (S), μV/K	Thermal conductivity (κ), W/m·K
$Pb_{16}Sn_2Ag_2Te_{20}$	270	300	200	1.5
$Pb_{16}Sn_2Ag_2Te_{20}$	1080	200	250	0.8
$Pb_{17}Ag_2Te_{20}$	405	180	-218	2.8
$Pb_{17}Ag_2Te_{20}$	270	205	-198	3.0

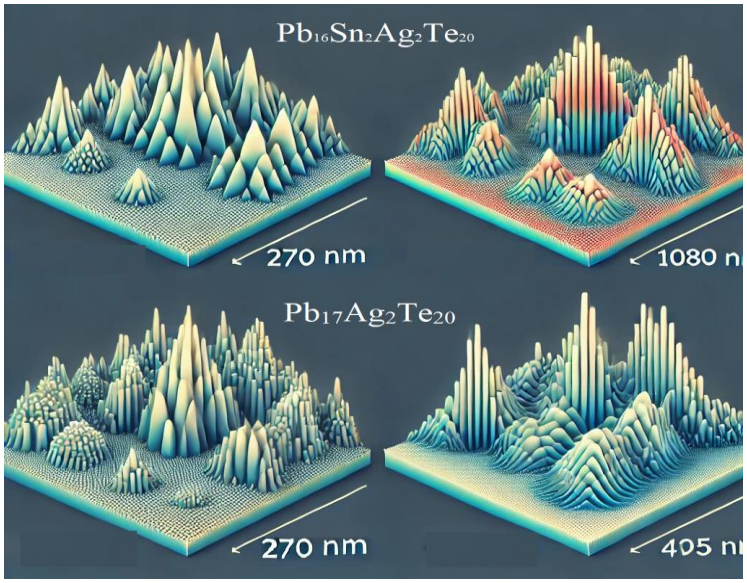

Fig. 2. The image depicts four surfaces generated by AI as a result of modeling with nanocrystallites for the films $Pb_{16}Sn_2Ag_2Te_{20}$ and $Pb_{17}Ag_2Te_{20}$, obtained on sitall substrates.

edges and smooth peaks. The sizes in the normal direction are quite small, around ~14 nm. As the film thickness increases to ~0.5 μm, the structure of the films becomes non-uniform, with a predominance of grains in the shape of flat truncated pyramids with a height of ~5 nm and a base of 300-500 nm. Against this background, there are individual grains with a height of ~20 nm, sharp peaks, and a base of 80-100 nm [7].

Conclusions

For thermoelectric applications, it is better to use thicker films (~1000 nm), which have higher thermoelectric efficiency due to reduced thermal conductivity.

For electronic devices where high electrical conductivity is important, films with a thickness of 200-300 nm and smaller grains are optimal.

Based on the modeling results, the film deposition process can be automated to achieve the desired characteristics. The XGBoost model can be used in real-time to predict the optimal film thickness and deposition time depending on the desired electrical properties.

Applications with high requirements for the thermoelectric coefficient (S) and low thermal conductivity (κ) require the use of thicker films (approximately 1000 nm or more), as this leads to an increase in the thermoelectric coefficient and a decrease in thermal conductivity. Recommended thickness: 800-1200 nm.

For devices with high electrical conductivity: If maximum electrical conductivity is needed (e.g., for sensors or contacts), it is better to use thinner films (up to 300 nm), where the grain height is smaller, which contributes to better electrical conductivity. Recommended thickness: 200-300 nm.

Addition. Part of the XGBoost simulation code:

```
import xgboost as xgb
from sklearn.model_selection import train_test_split
from sklearn.metrics import mean_squared_error, r2_score

# Data
X = [[35, 270], [80, 1080], [60, 405], [35, 270]]

y_H = [8.8, 11.47, 13.67, 14.05]
y_Sa = [1.05, 1.34, 1.23, 1.86]
y_Sq = [1.42, 1.69, 1.75, 2.27]
y_D = [35.5, 32.9, 150, 100]
y_sigma = [2.8, 3.2, 4.1, 5.0]  # Електропровідність (σ), S/cm
y_S = [210, 250, 270, 300]  # Коефіцієнт термоелектричного ефекту (S), μV/K
y_kappa = [1.5, 1.7, 2.1, 2.3]  # Теплопровідність (κ), W/mK

# Division of data into training and test sets
X_train, X_test, y_H_train, y_H_test = train_test_split(X, y_H, test_size=0.2, random_state=42)
X_train_Sa, X_test_Sa, y_Sa_train, y_Sa_test = train_test_split(X, y_Sa, test_size=0.2, random_state=42)
X_train_Sq, X_test_Sq, y_Sq_train, y_Sq_test = train_test_split(X, y_Sq, test_size=0.2, random_state=42)
X_train_D, X_test_D, y_D_train, y_D_test = train_test_split(X, y_D, test_size=0.2, random_state=42)
X_train_sigma, X_test_sigma, y_sigma_train, y_sigma_test = train_test_split(X, y_sigma, test_size=0.2, random_state=42)
X_train_S, X_test_S, y_S_train, y_S_test = train_test_split(X, y_S, test_size=0.2, random_state=42)
X_train_kappa, X_test_kappa, y_kappa_train, y_kappa_test = train_test_split(X, y_kappa, test_size=0.2, random_state=42)

# A function for model training, prediction and evaluation
def train_and_evaluate(X_train, X_test, y_train, y_test, label):
    Model creation and training
    model = xgb.XGBRegressor(n_estimators=100, learning_rate=0.05, max_depth=3)
    model.fit(X_train, y_train)

    # Prognostication
    y_pred = model.predict(X_test)

    # Evaluation of the model
    rmse = mean_squared_error(y_test, y_pred, squared=False)
    r2 = r2_score(y_test, y_pred)

    # Output of results
    print(f"RMSE для {label}: {rmse}")
    print(f"R2 для {label}: {r2}")
    print(f" {label}: {y_pred}")
    print(f" {label}: {y_test}")
    print('-' * 50)

    # Models for each parameter
    train_and_evaluate(X_train, X_test, y_H_train, y_H_test, "H")
    train_and_evaluate(X_train_Sa, X_test_Sa, y_Sa_train, y_Sa_test, "Sa")
    train_and_evaluate(X_train_Sq, X_test_Sq, y_Sq_train, y_Sq_test, "Sq")
    train_and_evaluate(X_train_D, X_test_D, y_D_train, y_D_test, "D")
    train_and_evaluate(X_train_sigma, X_test_sigma, y_sigma_train, y_sigma_test, "σ")
    train_and_evaluate(X_train_S, X_test_S, y_S_train, y_S_test, "S")
    train_and_evaluate(X_train_kappa, X_test_kappa, y_kappa_train, y_kappa_test, "κ")
```

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В.І. Маковишин, Т.Р. Стисло, О.О. Іванов, О.В.Стисло

Моделювання товщинних залежностей електричних параметрів та формування наноструктури у парофазних конденсатах сполук LAST за допомогою машинного навчання

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У статті розглядається моделювання товщинних залежностей електричних параметрів тонких плівок на основі сполук LAST (Pb-Ag-Sb-Te) із використанням методів машинного навчання. Метою роботи є оптимізація процесу осадження парофазних конденсатів для покращення термоелектричних властивостей матеріалів. Основну увагу приділено вивченню впливу товщини плівок та розмірів нанокристалітів на електропровідність та рухливість носіїв заряду. У статті вперше застосовано методи машинного навчання для прогнозування електричних параметрів на основі експериментальних даних. Для цього використовувалася модель XGBoost що дозволяє передбачати поведінку електропровідності та інших параметрів залежно від зміни товщини плівок, що сприяє підвищенню ефективності процесу їх формування. Результати дослідження показують, що правильна оптимізація параметрів осадження може значно покращити термоелектричні характеристики матеріалів, що важливо для застосування в енергетичних і електронних пристроях. Таким чином, стаття демонструє потенціал машинного навчання як інструмента для поліпшення технологічних процесів у виробництві наноструктурованих плівок сполук LAST.

Ключові слова: LAST, XGBoost, машинне навчання.