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Nanostructured $NaBiTe_2$ Thin Films and Their Properties

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The paper reports our experimental data on growth, morphology, optical and electrophysical properties of $NaBiTe_2$ thin films grown by thermal evaporation in vacuum. The structural characteristics and electric field-induced properties of semiconductor $NaBiTe_2$ films with Cr contacts are investigated. Room-temperature time dependence of the current flowing through the investigated structures under applied electric field is also discussed. The influence of some aggressive atmospheric impurities on $NaBiTe_2$ films characteristics is described for the first time.

Keywords: Thin films, Chalcogenide, $NaBiTe_2$, Structure, Surface relief, Optical transmission, Electric properties, Current mechanisms, Gas sensitivity.

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1. INTRODUCTION

Thin films of complex ternary chalcogenide compounds are characterized by a wide range of physical and chemical properties. Nevertheless, the various investigations of such materials were rarely carried out with using an opportunity to obtain systematic information about the subject of the study. Two main factors should be noted: i) only relatively small number of chalcogenide materials may be evaporated producing a stoichiometric film. The deviations from stoichiometry observed experimentally led to sufficient changes of necessary characteristic of the sample; ii) self-organization processes which are typical for complex multicomponent systems cause the phase transitions leading to oxidation, amorphous phase crystallization, time evolution of stoichiometry, etc. [1].

As it is known, crossing from elementary Group IV crystal semiconductor Ge and Si to similar binary compounds $A^{III}B^{V}$ (A = Ga, In, B = As, Sb, Bi) brings more complex crystal structures and ionic components of the chemical bonds due to appearance of two sorts of ordered atoms. Further complication of chemical composition in ternary compounds causes change of atoms in the cation sublattice resulting in new physical properties. Therefore, their structural, optical and electric properties attract special interest of researchers working in field of nanotechnology and nanoelectronic applications [2-4].

Earlier we have studied electric field-induced characteristics of $NaSbSe_2$ [5].

The presence of chalcogene element makes it possible to affect the stability and sensitivity to ambient environment of the respective thin films creating a perspective for using them as active elements of sensor devices [6].

The paper describes experimental results on growth, structure, optical and electric field-induced characteristics of thin films prepared from $NaBiTe_2$ chalcogenide semiconductor. This compound crystallizes in NaCl-like cubic lattice with parameter a = 0,639 nm.

2. EXPERIMENTAL

$NaBiTe_2$ thin films with different thicknesses (60 – 200 nm) were deposited on glass substrates from Knudsen cell under vacuum level $P = 10^{-3}$ Pa. The average rate of deposition was operated by change of the evaporator temperature and estimated to be 0.1 – 0.5 nm/s. The area of the samples was measured to be $6 \times 32 mm^2$, the distance between electrodes had not exceeded 30 mm.

The microstructure and phase composition of the films have been studied by transmission electron microscopy (TEM) and diffraction methods.

AFM investigations of as-grown samples and after NO exposition were carried out.

Two sets of $NaBiTe_2$ samples were prepared: with Cr contacts for electric studies and without them for optical investigations. To provide maximum accuracy of the electric measurements focusing on $NaBiTe_2$ films, the investigated layers were deposited on the substrates with Cr contact pads previously prepared by vacuum resistive evaporation. Before Cr deposition the substrates were chemically treated and then heated in vacuum in the temperature range 600-700 K. The thickness of the chromium pad was about 1000 nm.

Studies of the electric field-induced properties were carried out in vacuum (in the growth chamber *in situ*) as well as in open air at normal atmospheric conditions and under applied electric field up to 10^5 V/m.

3. STRUCTURAL INVESTIGATIONS

Two sets of films were selected for structural studies: the first family of as-grown layers (glass substrate, T_s = 300 K) and the second group of specimens deposited on the glass substrate at the room temperature after annealing in air under normal atmospheric conditions.

As is shown in Fig.1, the film microstructure is characterized by presence of small disperse particles. The microcrystalline phases are good seen in the electron-diffraction patterns. The electron beam-induced anneal leads to the film crystallization and re-evaporation of tellurium. After annealing in air under

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normal atmospheric conditions at T = 373-393 K nanocrystals Bi_2Te_3 and $NaTe_3$ as well as nanoparticles are observed (see Fig. 2).

The heat treatment of the films in air is accompanied by the formation of BiO_3 and TeO_2 oxides.

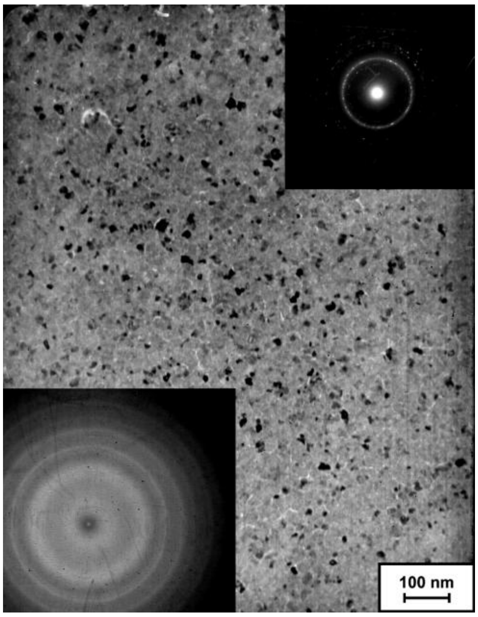


Fig. 1 – TEM image, diffraction and microdiffraction patterns of the $NaBiTe_2$ films with 30 nm thickness deposited on the glass substrate at T_s = 300 K under deposition rate 0.1 nm/s (the original sample)

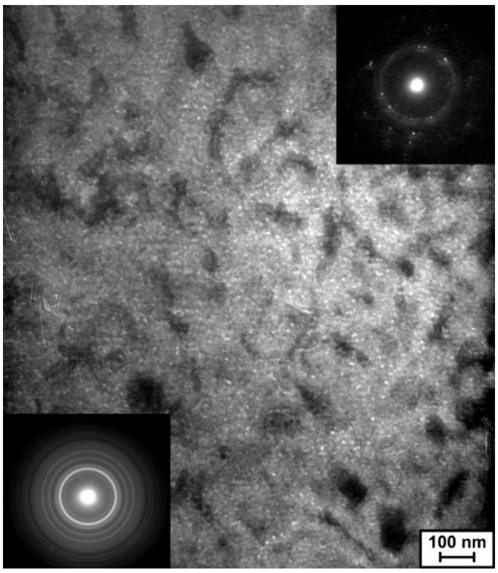


Fig. 2 – TEM image, diffraction and microdiffraction patterns of the $NaBiTe_2$ films with 80 nm thickness deposited to the glass substrate at T_s = 300 K under deposition rate 0.5 nm/s after annealing in air under normal atmospheric conditions

4. RESULTS OF ELECTRICAL MEASUREMENTS AND THEIR DISCUSSION

Electrical measurements were performed at the room temperature under applied electric field up to 10^4 V·m^{-1}. The current-voltage characteristic of the film is illustrated by the Fig. 3.

As it is shown, this dependence is of exponential character typical for metal-semiconductor structures. Such a characteristic may be qualitatively described as follows:

$$j(E) \sim j_0 \exp[(eEd_{tun} + \Delta)/k_B T], \quad (1)$$

where E is the applied electric field, d_{tun} is the distinctive tunneling length, Δ is the tunneling parameter defined numerically, and j_0 stands for a saturation current [7].

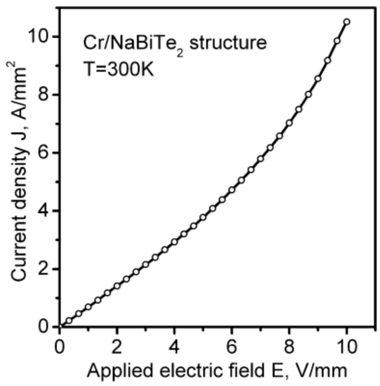
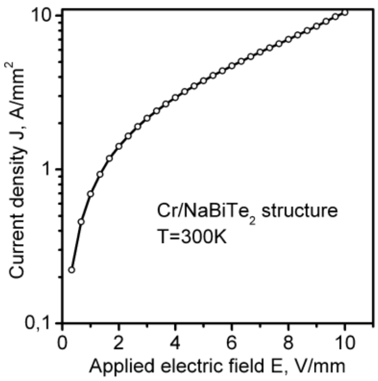
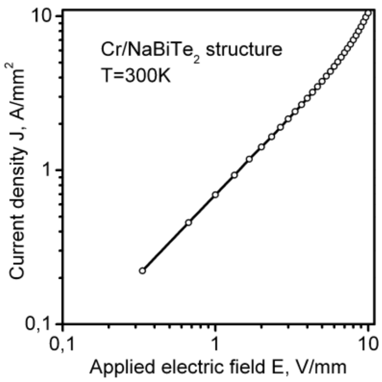


Fig. 3 – Room-temperature current-field characteristic of the investigated sample (Cr-contacts)

For more detailed study of current mechanisms in the investigated structure the experimental curve was rebuilt in semi-log and double log scales (Fig. 4, a, b).



a



b

Fig. 4 – Semi log current-field characteristic of the investigated sample (Cr-contacts) (a) and double-log one (b)

Double-log recalculation of the experimental current-voltage dependence shows the smooth superposition of at least three modes of the carriers transport:

- current caused by the carriers injected from the metallic contact under the applied voltage 50-100 V [8];
- velocity-saturation regime under the applied voltage up to 120 V, where $I \sim (2\varepsilon\varepsilon_0 \upsilon_{sat} V_a/L^2)$, υ_{sat} is determined from the experimental data and L is the thickness of the film;
- The current governed by so-called "3/2"-law as the applied voltage increases: $I \sim (4\varepsilon\varepsilon_0/9L^2)(2e/m^*)^{1/2}(V_a)^{3/2}$.

The time evolution of the film conductivity is also interesting. Fig. 5 illustrates this dependence for the as-grown films. As is shown (Fig. 5), the conductivity of the film rapidly decreases during first 30 min of measurement and then monotonously decreases during following 50 min.

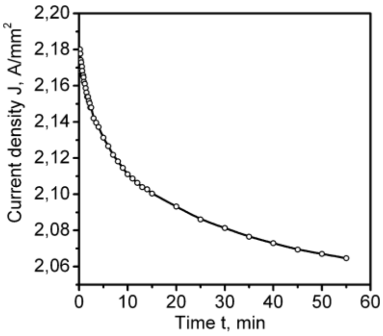


Fig. 5 – Time dependence of the current flowing through the investigated $NaBiTe_2$ film in vacuum after its preparation

The experimental dependence $j(t)$ can be qualitatively described as

$$j(t) \sim j_0 \cdot \exp(-t/\tau), \quad (2)$$

where j_0 and τ are the initial current density and so-called stabilizing time, respectively. Both terms are functions of the film parameters *in vacuum* (the carriers' mobility and scattering mechanism on the surface relief are crucial).

5. GAS SENSITIVITY INVESTIGATIONS

Optical and surface properties before and after NO exposure were studied.

In order to examine gas sensitivity the as-grown films were placed in the closed chamber with different NO concentration at the room temperature.

Fig. 6 plots experimental transmission spectra of the investigated samples after interaction with nitrogen monoxide of various concentrations. As is shown, the films demonstrate significant changes of their optical characteristics even at low concentrations of the aggressive gas. As the nitrogen monoxide concentration increases, the transmission of the examined layers is also increasing (Fig. 6).

After the NO exposition the film relief is significantly changed.

Fig. 7 presents the typical AFM image of the as-grown sample (a) and after NO exposure (b). The standard image numerical processing enabled to estimate the parameters of the surface roughness (Table 1), where:

R_a is a medial roughness of profile;
R_q is a root-mean-square roughness of profile;
R_z is a medial roughness of a profile on 10 points.

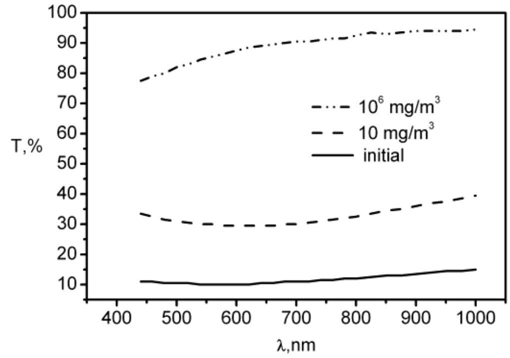
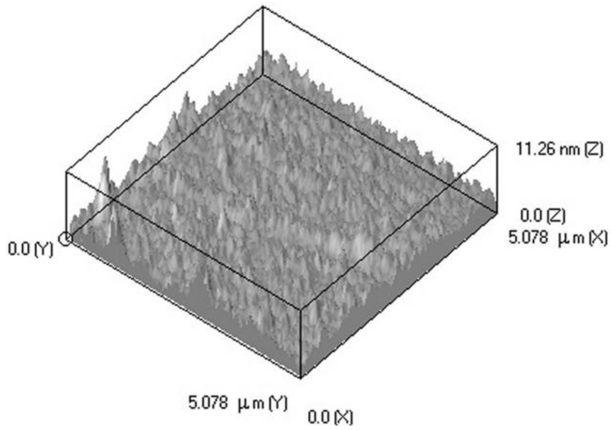
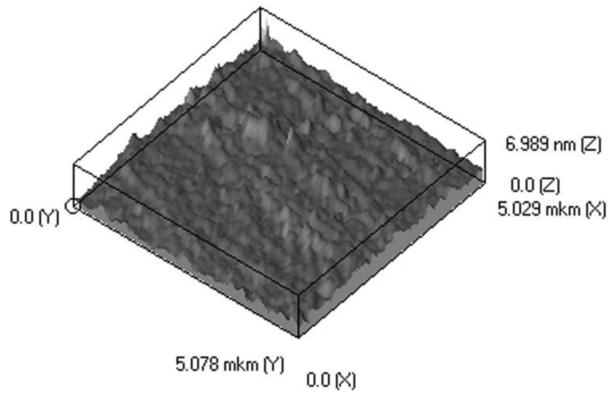


Fig. 6 – Transmission spectra of the original $NaBiTe_2$ film and after nitrogen monoxide exposure under concentration: 10 mg/m^3 and 10^6 mg/m^3 during 60 min, sensor operating temperature 300 K



a



b

Fig. 7 – AFM image of $NaBiTe_2$ film surface (the as-grown sample) (a) and after NO exposure (b)

Table 1 – Roughness of $NaBiTe_2$ film surface before and after NO exposition

Roughness	Initial	No
R_a, nm	0.9	0.3
R_q, nm	1.2	0.5
R_z, nm	5.5	1.9

Another important question is how the conductivity of the films changes under exposure of different aggressive environments. The time profile of the DC current flowing through the sensor in response to adsorption and desorption of different gases as a very important characteristic of the device [9] had been also investigated.

Fig. 8 demonstrates current response curves measured after undergoing the examined samples to sulfur hydroxide (a) and NH_3 (b) gas exposure at the room temperature. These data point out sensitivity and response of the films to NH_3 and H_2S exposure. As one can see, the reversible adsorption takes place, but the problem of time stability is to be solved. So that, this material appears to be perspective in gas sensors development.

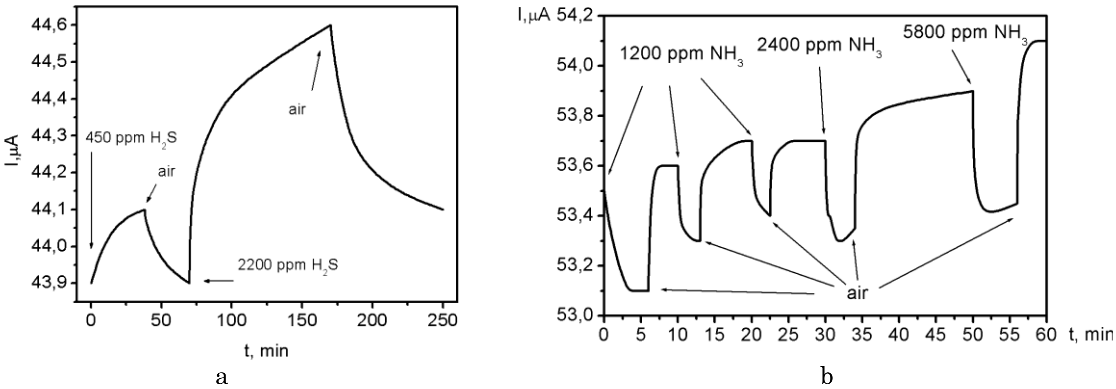


Fig. 8 – Current response of the investigated $NaBiTe_2$ thin film at different concentration of H_2S (a) and NH_3 (b), sensor operating temperature 300 K

6. CONCLUSIONS

We yielded $NaBiTe_2$ thin films on glass substrates.

The structure of our samples is microcrystalline with typical grain size about 30 nm. Anneal leads to the film recrystallization, evaporation of tellurium and oxidation.

Charge transport mechanism was also investigated. It was determined that time dependence of the film conductivity under applied DC electric field is caused by different processes of the carriers' injection and surface recombination. Room-temperature current-voltage characteristics revealed a smooth superposition of drift-diffusion current, velocity saturation mode and ballistic regime at the all range of applied voltage (0-140 V).

The influence of some aggressive gases on $NaBiTe_2$ films properties was studied for the first time. The optical transmission and surface relief changes under interaction with NO. Adsorption of such atmospheric impurities as H_2S and NH_3 result in conduction drift.

So $NaBiTe_2$ thin films appear as perspective objects for gas sensors development.

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Наноструктурные тонкие плёнки $NaBiTe_2$ и их свойства

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В статье представлены наши экспериментальные результаты по росту, морфологии, оптическим и электрофизическим свойствам тонких пленок $NaBiTe_2$, выращенных термическим испарением в вакууме. Изложены результаты структурных исследований и электрических измерений пленок $NaBiTe_2$ с Cr контактами. Также обсуждаются временные зависимости тока, протекающего через исследуемые структуры при постоянном приложенном электрическом поле при комнатной температуре. Впервые описано влияние некоторых агрессивных атмосферных примесей на характеристики пленок $NaBiTe_2$.

Ключевые слова: Тонкие плёнки, халькогениды, $NaBiTe_2$, структура, поверхностный рельеф, оптическое пропускание, электрические свойства, механизмы зарядопереноса, газовая чувствительность.

Наноструктурні тонкі плівки NaBiTe$_2$ та їх властивості

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У статті представлені наші експериментальні результати по росту, морфології, оптичним і електрофізичним властивостям тонких плівок NaBiTe$_2$, що було вирощено термічним випаром у вакуумі. Докладені результати структурних досліджень та електричних вимірів плівок NaBiTe$_2$ з Cr контактами. Також обговорено часові залежності струму, що тече через ці структури при постійному прикладеному електричному полі при кімнатній температурі. Вперше описано вплив деяких агресивних атмосферних домішок на характеристики плівок NaBiTe$_2$.

Ключові слова: Тонкі плівки, халькогеніди, NaBiTe$_2$, структура, поверхневий рельєф, оптичне пропущення, електричні властивості, механізми зарядопереносу, газова чутливість.

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