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Peculiarities of Bi$_4$Ti$_3$O$_{12}$ films grown by DC magnetron sputtering

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Abstracts. — The peculiarities of the synthesis and crystallization of complex oxides (Bi$_4$Ti$_3$O$_{12}$ as an example) from the decay products in magnetron sputtering are discussed. The processes of complex oxide sputtering by ion bombardment, transfer of the products through the plasma to the substrate, the surface processes on the substrate and oxidation-reduction processes are considered. The dynamics of the layer formation is investigated by measuring the spectral line intensities ($\lambda_{Bi} = 472.25$ nm and $\lambda_{Ti} = 498.1$ nm) of the sputtered atoms at the target surface. The film deposition mechanism is shown to change with distance between substrate and target. A critical distance of $h_{crit} = 7$ nm is found. At $h < h_{crit}$ atoms are deposited, while at $h > h_{crit}$ molecules condense. The degree of crystallization depends on oxygen pressure. Thermal activation strongly affects the deposition rate. In the case of molecular deposition at temperatures of $\approx 900$ °C the high-temperature phase of $\gamma$-Bi$_2$O$_3$ forms along with Bi$_2$O$_3$ and TiO$_2$. The dielectric loss tangent of Bi$_4$Ti$_3$O$_{12}$ films depends on the bias potential of the substrate.

1. Introduction.

Due to a lack of reliable method of the complex oxide film growing and imperfect understanding of physico-chemical processes of their growth, the fundamental studies of such films and their practical application are retarded.

Up to the present the main directions of films production (vacuum evaporation, explosive or «pulse» evaporation [1], two-electrode cathode sputtering with dc, cathode sputtering with a radio-frequency [2]) are formulated, and the variations of the conditions of film formation (the velocities of compound deposition and the substrate temperature, the composition and plasma-forming gas pressure) are known, and the composition, structure, morphology of empiric parameters of layers and the optimization of the conditions of their formation are studied. Really, such an approach essentially ignores the phenomena occurring during evaporation and sputtering in terms of physics and chemistry, and is hardly justified in case of noncongruently evaporated compounds of complex metal-oxide type. Due to this fact, it is reasonable to study physical and chemical processes occurring on target, in plasma and on the substrate. There is a number of works [3, 4] where a mass-spectroscopic investigations of the vapour composition at a gradual and «pulse» heating of BaTiO$_3$ to different temperatures are discussed. It is
appeared that Ba\textsuperscript{+}, BaO\textsuperscript{+}, Ti\textsuperscript{+}, TiO\textsuperscript{+} and TiO\textsubscript{2} are present in vapours, and a weak ionic current formed by BaTiO\textsubscript{3} is also registered. It is assumed that there is a possibility of existence of more heavy clusters which are ionized without dissociation and therefore they are not recorded.

As far as we know, there is no similar data for the case of dc magnetron sputtering. Therefore the spectroscopy studies of kinetics processes in plasma of sputtering device of dc magnetron system has been carried out, and the experimental data on the peculiarities of synthesis and crystallization of complex oxides (Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} as an example) from the decay products at dc magnetron sputtering are discussed in the present paper. Conventionally the layer growing process is divided into the following stages: the complex oxide sputtering under the effect of ionic bombardment; the transfer of the products through the discharge plasma to the substrate; the surface processes on the substrate: oxidation-reduction processes.

2. Experimental.

2.1 Sputtering and Measurement Technique. — Both the process of the formation of thin films and the reliability of results of their further investigation are primarily determined by conservation of stoichiometric ratio of atomic components of complex oxide.

A vacuum condensate composition is mainly determined by the condition of the formation of layer, changed in its composition, on the surface of target depleted in component with a large sputtering coefficient. In case of diffusion fluxes in a target substance at the given temperature this process leads to the establishment of quasiequilibrium state when the ratio of the component concentration in a surface layer of the target is inversely proportional to the corresponding sputtering components that provides the entering of components to a working medium in a stoichiometric ratio.

The Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} plate obtained by a hot compacting of Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} powder of a stoichiometric composition was used as a target. The mixture of Ar and O\textsubscript{2} was used as a working medium. The structure of the obtained films were investigated using electron diffractometer EP-100 and electron microscope EM-14. The chemical composition of films was determined by local X-ray spectral method on scanning electron microscope REM-101 M by comparison of spectral line intensity relations for films and standard sample. The experimental studies of the layer formation dynamics were carried out on the base of the spectral line relative intensity measurements (\(\lambda_{\text{Bi}} = 472.25\) nm and \(\lambda_{\text{Ti}} = 498.1\) nm) of the sputtered atoms at the target surface. A principal scheme of the setup is shown in figure 1. The system of lenses and mirrors (9) allows to obtain the image of target and discharge in the plane of monochromator slit (10) which cuts off a part of the radiation source image. This fact in turn allows to study the spectrum of a narrow part of discharge rather than the source as a whole. Appropriate region of discharge was separated by scanning of monochromator slit with height. A signal passed through the monochromator and the selective amplifier was treated on electron computer and was recorded on the device. During experiments the pressure in jet chamber was prescribed by the balance of rates of pumping and supply of working gas (oxygen or argon).

The lines of neutral atoms of Bi and Ti (identification of Bi and Ti lines was carried out on sputtering of pure Bi and Ti in argon atmosphere) and the wide bands corresponding to BiO, Bi\textsubscript{2}O\textsubscript{3}, TiO, TiO\textsubscript{2} molecules were observed in discharge spectra. The measurement of the ratio of the sputtered atom concentration \(N_{\text{Ti}}/N_{\text{Bi}}\) with time was fixed as the change of \(I_{\text{Ti}}/I_{\text{Bi}}\). In the first stage (~30 min) of the target sputtering this dependence has the form shown in figure 2. The behaviour of this dependence indicates that the sputtering coefficient of Bi is larger as compared to that of Ti. As a result, the surface layer of the target is enriched by titanium. These data are in a good agreement with the results of calculation of Bi and Ti bonding energy in Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} crystal [5].
3. Results and discussion.

3.1 The transfer of decay products. — The dependence of Bi line intensities, $\text{Bi}l_\lambda = 472.25$ nm, on distance to the target $h$ is shown in figure 2, curve 1.

As seen in figure 2, the intensity curve has a certain maximum. However, this dependence does not reflect the distribution of Bi atom concentration in the discharge as spectral line intensity, except for the amount of atoms radiating the photons of a certain energy, also depends on conditions of excitation which can change with distance variation. Therefore, the dependence of a relative intensity of oxygen lines, $\text{O}l_\lambda = 436.8$ nm, on the distance to the target (Fig. 2, curve 2) has been studied.

The following equations can be written for bismuth and oxygen spectral line intensities:

$$I_{\text{Bi}} = K_{\text{Bi}} N_{\text{Bi}}$$  \hspace{1cm} (1)

$$I_{\text{O}} = K_{\text{O}} N_{\text{O}}.$$  \hspace{1cm} (2)

Here $N_{\text{Bi}}$ and $N_{\text{O}}$ are the concentrations of atoms; $K_{\text{Bi}}$ and $K_{\text{O}}$ are the coefficients depending on conditions of line excitation. Assuming approximately that the potentials necessary for

Fig. 2. — The dependence of radiation intensity of Bi and O atoms (curves 1 and 2) and the Bi atom concentration (curve 3) on the distance to the target.
excitation of Bi, Ti and oxygen atoms are similar, one can consider that \( K_{\text{Bi}} = K_{\text{Ti}} = K_O \). Hence,
\[
\frac{I_{\text{Bi}}}{I_O} = \frac{N_{\text{Bi}}}{N_O}
\] (3)

A similar equation can be written for titanium
\[
\frac{I_{\text{Ti}}}{I_O} = \frac{N_{\text{Ti}}}{N_O}
\] (4)

As the concentration of oxygen atoms in working volume is considerably larger that of oxygen atoms removed from the target, the oxygen atom concentration \( N_O \) can be considered as a constant value in time.

Then, within the framework of above assumption the concentration of Bi and Ti atoms is determined by the equations (3), (4), respectively. The distribution curve of Bi atom concentration in the discharge has the form shown in figure 2 (curve 3). As seen from the curve, the Bi atom concentration is nearly independent of distance close to the target, and then sharply decreases. The beginning of decay of the concentration curve (3) coincides in this case with the maximum of the intensity curve (1). As the radiation intensity of Bi atoms near the target is non-zero, it means that the atoms removed from the target are excited.

As the amount of oxygen in plasma forming gas composition changes (the change of partial pressure of \( O_2 \)), the behaviour of the intensity line of Bi and Ti atoms also changes (Fig. 3). Except for the lines of neutral atoms, there exist the bands corresponding to BiO, TiO and \( O_2 \) molecules in the spectra. With increasing the distance from the target the line intensity of BiO and TiO increases, while for Bi and Ti atoms the distance has been found to decrease. These data as well as the decrease of the line intensity of Bi with increasing oxygen pressure in a working medium allow to confirm that at collision of Bi and Ti atoms with oxygen atoms the chemical reactions, the products of which are BiO and TiO oxides, occur in plasma. This fact probably leads to a sharp decrease in intensity of atomic lines of Bi and Ti with increasing distance from the target.

As a rule, at distance from target \( h < h_{\text{crit}} \) the radiation intensities of the corresponding molecular bands of \( \text{Bi}_2\text{O}_3 \) (BiO), TiO and TiO2 are on the level of plasma noises. A sharp decrease of atomic bands at \( h < h_{\text{crit}} \) is accompanied by increase in radiation intensity of BiO molecular bands.

![Image](image.png)

Fig. 3.— The dependence of Bi and Ti atom radiation intensity on the plasma forming gas pressure.
The presence of critical distance $h_{crit}$ can be explained by the fact that the energy of sputtered atoms is about tens of electron-volts and exceeds the dissociation energy of BiO (as an example) equal to 6 eV [5, 6]. Therefore the formation of BiO molecule is impossible until the Bi atoms transfer the excess energy to atoms of plasma forming gas. This fact explains the great dependence of critical distance on the plasma forming gas pressure.

One can assume that the distribution of bismuth atom concentration and of the bismuth oxide observed experimentally is due to dependence of the cross-section of the oxide formation on the relative velocity of bismuth and oxygen atoms. At different distances from the sputtered electrode the Bi atom velocity decreases and the probability of the oxide formation increases respectively.

Another variant consists in the change of conditions determined by free path length of Bi with respect to reaction of bismuth oxide formation.

A quantitative description is based on steady-state continuity equation when the decrease of bismuth concentration ($n$) and the increase of its oxide concentration ($p$) are only due to reaction of oxide formation (with a characteristic time $\tau$).

\[
\frac{d}{dx} n v_n = -\frac{n}{\tau} \\
\frac{d}{dx} p v_p = \frac{n}{\tau}
\]  

(5)

($v_n$ and $v_p$ are the rates of bismuth atom and bismuth oxide, respectively, which are considered to be constant).

The boundary conditions for the system (5) are

\[ n(0) = n_0 ; \quad p(0) = 0. \]

When solving the system, we obtain

\[
n(x) = n_0 e^{-\frac{x}{\tau v_n}} \\
p(x) = n_0 \frac{v_n}{v_p} \left(1 - e^{-\frac{x}{\tau v_p}}\right).
\]

(6)

(7)

Experimentally the transition (through coordinate) from bismuth radiation to the radiation of its oxide is observed.

The equation for determination of the above distance from the sputtered electrode can be obtained from (6) and (7):

\[ p(x) = n(x) \]

(8)

Then,

\[ x_0 = \tau v_p \ln \left(1 + \frac{v_p}{v_n}\right). \]

(9)

Note that at inelastic collision of bismuth and oxygen the law of conservation of momentum takes place

\[ m_n v_n + m_k v_k = (m_n + m_k) v_p. \]

Here $m_k$ is a mass, and $v_k$ is the velocity of oxygen. By averaging we obtain the following
expression (taking into account that $v_k = 0$):

$$\frac{v_p}{v_n} = \frac{m_n}{m_k + m_n} \quad (10)$$

Substituting (10) into (5) we have

$$x_0 = \tau v_n \frac{m_n}{m_k + m_n} \ln \left(1 + \frac{m_n}{m_k + m_n}\right). \quad (11)$$

Thus, we obtain the expression for critical length ($h_i \equiv x_0$) through parameters of our system.

As seen from (7), $x_0$ is proportional to emission energy of Bi atom determined in turn by bombardment energy.

In the case when the length, at which the velocity of bismuth atom decreases up to the value when the reaction is possible, is much larger than $x_0$, the above formula yields not a distance from the sputtered electrode but a width of transition through the coordinate from bismuth to its oxide. Hence, versus the pressure and the gas composition, and also the distance between the target and the substrate, two mechanisms of the complex oxide film growth determined by the character of adsorbing particles, i.e. atomic or molecular, are possible.

3.2 PROCESSES OCCURRING ON THE SUBSTRATE. — As is known, the velocity of the metal film growth decreases with increase of the substrate temperature due to reevaporation. A similar dependence of the growth velocity on the substrate temperature is also observed in the case of the complex oxide film formation at the dc magnetron sputtering if the material considered is deposited in the form of atoms (Fig. 4, curve 1), $P = 0.1$ Torr, $h = 7$ mm.

At the deposition of material in the form of molecules the deposition velocity increases with the increase of the substrate temperature (Fig. 4, curve 2), $P = 0.3$ Torr, $h = 14$ mm. This is probably due to the fact that the reevaporation plays a secondary role (the accommodation coefficient of molecules is larger as compared to that of atoms) and the processes of synthesis and crystallization activated thermally acquire a dominant role.

A different mechanism of deposition determined by the character of depositing particles affects the composition and the structure of deposited layer. The electron diffraction pattern of Bi$_2$Ti$_3$O$_{12}$ films with thickness of $\sim 2$ μm obtained by magnetron sputtering on crystal substrates at temperatures of $\sim 700$ °C and different plasma-forming gas pressures are shown in

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Fig. 4. — The dependence of Bi$_2$Ti$_3$O$_{12}$ film growing velocity on the substrate temperature for two types of particle deposition: 1. atomic; 2. molecular.
figure 5. As seen in figure 5, the crystallization degree decreases with decay of oxygen pressure in a working chamber, i.e. at transition from the adsorption of molecules to that of the atoms. Note that the films obtained at $P = 0.1$ Torr (1 % O$_2$) are amorphous. During the film growth in such conditions when the deposited particles are the atoms and the reevaporation takes place, the probability of point defect formation and the stoichiometry disturbance is great. These structural defects of nucleations in turn make «the perfect crystallization» of diffusible particles difficult leading to fixation of interstitial atoms. This fact explains a certain

![Image a](image-a)

![Image b](image-b)

![Image c](image-c)

Fig. 5. — Electron diffraction patterns of Bi$_4$Ti$_3$O$_{12}$ obtained at different plasma forming gas pressures. $T_{\text{sub}} = 600$ °C. $d \sim 2$ μm. a) $\sim 0.7$ Torr; b) $\sim 0.4$ Torr; c) $\sim 0.1$ Torr.
increase of the unit cell parameters with increasing deposition temperature (Fig. 6). At high
temperatures of deposition ($\geq 900^\circ$C) stimulating the reevaporation and the increase of
surface mobility of the adsorbed atoms along with the reflections of Bi$_2$O$_3$ and TiO$_2$ the new
reflections corresponding to a high-temperature phase of $\gamma$-Bi$_2$O$_3$ occur on electron diffraction
patterns.

In the case of deposition of particles as the oxides the unit cell parameters decrease with the
growth of substrate temperature and no other types of phases are observed.

![Graph showing temperature dependence of Bi$_4$Ti$_3$O$_{12}$ unit cell parameters at atomic (1) and
molecular (2) mechanisms of growth.]

**Fig. 6.** — The substrate temperature dependence of Bi$_4$Ti$_3$O$_{12}$ unit cell parameters at atomic (1) and
molecular (2) mechanisms of growth.

### 3.3 Oxidation-reduction processes.

As is known, the titanium-containing complex oxides easily loose an oxygen [7, 8]. The reduction can take place on heating in vacuum or in a
reducing medium (e.g. hydrogen) [5]. The oxygen deficite leads to increase of electroconduc-
tivity and a radical change of characteristics of switching and transmission spectra [9, 10].

In the case of magnetron sputtering, when studying the oxidation-reduction processes
occurring on a substrate, the specificity of radiation-chemical reactions, the ionized oxygen
activity and some other discharge peculiarities should be taken into account. Note that the
oxidation is mainly determined not by the integral pressure of plasma-forming gas, oxygen,
but by the density of atoms at the condensate surface.

In the case of deposition on electrically isolated substrate, due to high mobility of electrons
as compared to that of ions, the substrate is charged negatively. The condensate is bombarded
by ions and fast electrons capable of overcoming the potential barrier. This bombardment
should affect the synthesis and the crystallization of the layer as it promotes the increase of the
adsorbed atom mobility, and the direction of oxidation-reduction reaction as well. To
determine the contribution of ionic and electron bombardment to oxidation-reduction process,
the conductive substrates (platinum, stainless steel) with the applied constant voltage of
additional source were used.

With the high negative bias potential values relative to plasma the degree of electron
bombardment is negligible while at the positive bias voltage the condensate is subjected to
intensive electron bombardment. The tangent of dielectrical losses of Bi$_4$Ti$_3$O$_{12}$ films
deposited at different bias potentials ($U_{bias}$) is shown in figure 7. As seen in figure 7, at the bias
potential values \( U_{\text{bias}} \gg 0 \) the tangent of dielectric losses increases that indicates a dominant contribution of reduction process in a deposited layer. The bombarding electrons practically do not transfer the kinetic energy to the condensate atoms (the mass ratio). Probably, the electrons with the energy of about tens of electron-volt are responsible for electron excitations weakening the bonds between the atoms of deposited layer thereby creating the conditions for their reevaporation. When deposited on the substrate at \( U_{\text{bias}} < 0 \) the bombardment of condensate with positive ions is observed. This fact determines the kinetics of oxidation-reduction process. The decrease of \( \tan \delta \) in this case indicates the predominance of oxidation process.

Thus one can conclude that there is great connection between the conditions of the complex metal-oxide film growth and the processes responsible for the transfer of the substance from the target to a substrate at a magnetron sputtering.

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Proofs not corrected by the authors.