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Sprayed substance transfer and hard-melting composition formation in ion plasma system

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Relation between characteristics of discharge and parameters of growing film when using ion-plazma methods of spraying has been shown at the example of magnetron spraying of TaB_2. Possibility of the modeling application for explanation of composition and properties of the films produced by such methods has been shown. Suggestions about the mechanism of formation and growth of hard-melting metal boride films have been made.

На примере ВЧ магнетронного распыления TaB_2 показана взаимосвязь между характеристиками разряда и параметрами нарастающей пленки при использовании ионно-плазменных методов напыления. Показана возможность применения моделирования для объяснения изменений состава и свойств пленок, полученных такими методами. Сделаны предположения о механизме образования и роста пленок боридов тугоплавких металлов.

1. Introduction

Production and investigation of the properties of thin nanocrystal films and coverings are urgent issues of modern condense-state physics. Composition and structure prediction of such objects is of current interest in this sphere. Theoretical models are being developed for this purpose [1, 2]. But they are effective mostly when the system is in thermodynamic equilibrium state. Prediction results substantially depend on the initial conditions (atom energy, their quantitative relation etc.), experimental determination of which is not always possible, particularly for neutral atoms composing more than 90 % from the whole condensation flow. Considering gas discharge processes (sprayed substance transfer from the target surface to the surface of condensation) can be of great help in such case.

2. Experimental technique

As in previous works [3–5], films where precipitated by HF magnetron dispersion at constant power of 400 W. The target was the disc sintered of TaB_2 powder, as the bases the glass-ceramic glass and steel plates as well as fresh chips of NaCl monocrystals were used. Produced films were investigated by X-ray, radiograph electron microscopy and by secondary ion mass-spectrometry. Distribution of film thickness on the surface of transparent base was measured by optical profile meter. Pressure of working gas (p) and distance between the target and the base were changed during experiments.

Modeling results of transfer was carried in out approaching once (without taking into account collective interactions) by Monte-Carlo method, principal possibility of which and some results were discussed earlier [3–5].

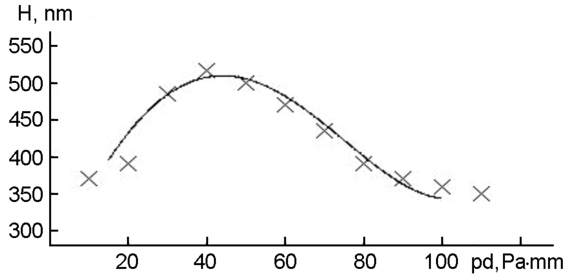

Fig. 1. Film thickness dependence on *pd* value, precipitation time being 30 min.

3. Results and discussion

All films obtained at given conditions grew with average speed of 2.3–2.7 A/c and were textured in the direction of <001>, that significantly obstructed X-ray investigation. But complex analysis defined them as being single-phase (TaB_{2-x}), having pronounced columnar structure, thin (10–20 nm) practically amorphous layer being on its surface. In our opinion, presence of the texture deals with processes of growth.

Change of argon pressure (p) from 0.18 to 0.72 Pa at constant distance $d = 120$ mm (or change of d at constant p) didn't cause significant difference of film structure, while their thickness and composition noticeably changed. So, film thickness being measured by X-raying ranged from 350–550 nm (Fig. 1), depending on the value of *pd*. As it has been shown by SIMS, relation of intensity of main mass peaks inside films fluctuated in the range of values B/Ta from 2.6 to 4.7, it being 5.1 in the target material. Such results could be explained by changing discharge characteristics (current of discharge, voltage on the target, ect.) causing differences of spraying conditions. But carried analysis enabled to make the conclusion about inessentiality of variation and influence (not more than 3–4 %) of discharge parameters. Besides it doesn't explain significant change of Boron quantity in supernatant layers (Fig. 2).

Carried modeling conditions of transfer helped to clarify understanding processes of formation and growth of films as understanding nature of found differences. Modeling data showing alteration of the whole quantity of condensed atoms (curve *1*) depending on *pd* value have been given in Fig. 3. However, obtained maxima on these curves are rather different from experimental. That is why separation of energy distribution has been done. Energy corresponding to heat one at melting point of TaB_2 has been taken as separation criterion. Curves *2* in the figures show atom distribution with the

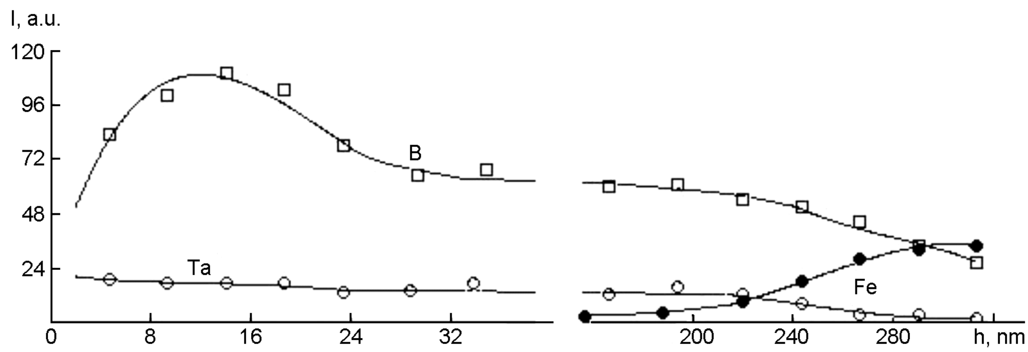

Fig. 2. Film mass spectrum having thickness 240 nm precipitated on a steel base.

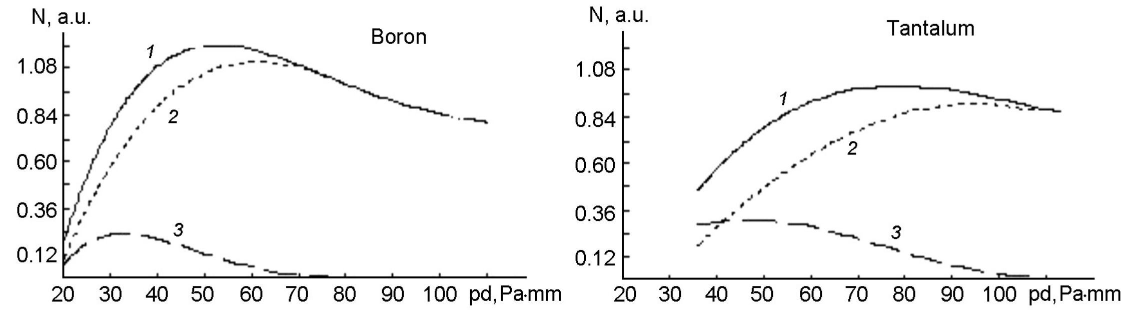

Fig. 3. Modeling B and Ta atom flows coming to the base.

"temperature" below melting point, curves *3* show atom distribution with the "temperature" above melting point.

Comparison of the experiment and modeling results gives reasons to assume that only a part of metal atoms, coming to the base with definite energy, take part in forming and growing boride films of hard-melting metals, while there is no such strict restriction for boron atoms. Such assumption is also confirmed by distribution character of film thickness on the base surface (Fig. 4), when it is distribution curve of Ta "hot" atoms that gives the best coincidence with the experimental results.

4. Comparing experimental results and modeling

It also can be supposed, that boride compound formation in this system occurs mainly because of diffusion of boron atoms from supernatant layers inside of growing film and that is why growth and formation of films is controlled by two parameters: energy of coming atoms and speed of their coming into adsorption layer. This fact explains some details: existence of practically amorphous layer of a film on the surface, a great amount of boron in it, some difference in composition of films grown at different speeds of growth and film structure practically identical to TaB_2. Boron diffusion coefficient in tantalum with diboride formation is known to be more than one order higher than for other tantalum borides.

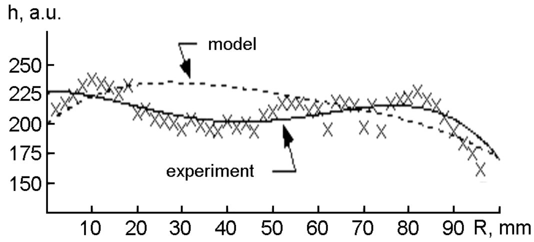

Fig. 4. Distribution of the film thickness on the base surface.

5. Conclusion

Thus, based on comparison of the results of modeling and experiment we can assume that such film formation occurs on the following mechanism: metal lattice is formed at first, only those neutral atoms that reach a base and have energy not less some value taking part in this process. Boride formation is controlled by boron solid-phase diffusion of boron from the supernatant layers into the film depth.

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Перенесення розпиленої речовини і формування тугоплавких сполук в іонно-плазмових системах

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На прикладі ВЧ магнетронного розпилення TaB_2 показано взаємозв'язок між характеристиками розряду і параметрами наростаючої плівки при використанні іонно-плазмових методів напилення. Показано можливість застосування моделювання для пояснення змінення складу і властивостей плівок, отриманих такими методами. Зроблено припущення про механізм утворення і зросту плівок боридів тугоплавких металів.