Cubic Solid-solution Ti$_x$Si$_y$N$_z$(O) Films: Synthesis, Structure and Electronic Properties

Mikhail V. Kuznetsov,* Elizaveta V. Shalaeva*, Sergei V. Borisov, Boris V. Mitrofanov, Alexander L. Ivanovsky and Gennady P. Shveikin

Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620219 Ekaterinburg, Russian Federation. Fax: +7 3432 444495

Monophase films of the metastable cubic phase Ti$_x$Si$_y$N$_z$(O) with the B1 structure have been synthesized; introduction of silicon atoms into the non-metallic sublattice of titanium oxynitride has been proved experimentally and theoretically.

Carbides, nitrides and oxides of IV–V group d-transition metals with the B1 structure and their solid solutions possess a unique set of properties combining high melting temperatures, hardness, radiation stability and a number of intriguing electromagnetic and spectral characteristics.[1,2] A new direction developed over the last few years in the modification of the composition and properties of these metal-like phases, which are characterized by a covalent-ionic-metallic type of chemical interaction, is the introduction of 3p-elements (Al, Si), whose nitrides (carbides) are non-isostructural with d-metal nitrides and which have a predominantly covalent type of chemical bonding, into the B1-lattice. According to experimental data available and theoretical quantum chemical calculations performed, the solid solutions Ti$_x$Al$_{1-x}$N, Ti$_x$Si$_y$N$_z$ (B1 structure type) are metastable and, therefore, can only be realized under non-equilibrium synthesis conditions, for instance, in the form of films in ion-plasma vapour deposition. A great number of works are now devoted to the synthesis, structure and properties of Ti$_x$Al$_{1-x}$N solid solution films.[3–7] The problems of the possibility and conditions of formation, the structure and stability of the cubic phases Ti$_x$Si$_y$N$_z$ and Ti$_x$Si$_y$N$_z$(O) remain to be explored.

Ti–Si–N(O) films have been made by an arc-method[8,9] using the Ti$_{0.7}$Si$_{0.3}$ target. The working gas (N$_2$) pressure, substrate temperature and negative potential on the substrate were varied in the process of deposition. The films were examined by X-ray photoelectron (XPS) and Auger-spectroscopy (VG ESCALAB MKII), by X-ray probe microanalysis (JCXA-733) and by transmission electron microscopy (JEM-200C).

As a result it has been shown that within a narrow range of nitrogen pressure $P(N_2) = 6 \times 10^{-2}$–$1 \times 10^{-1}$ Pa the Ti$_x$Si$_y$N$_z$(O) films deposited by an arc-method at substrate temperature $T = 470$ K have a monophase cubic structure of the B1 type [Fig. 1(a)]. X-ray probe microanalysis has given support to the uniform distribution of silicon atoms in the
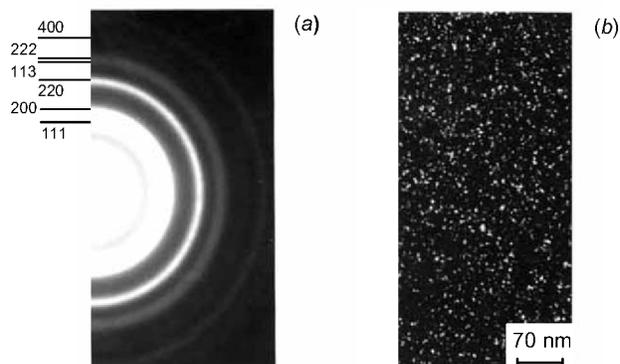

Fig. 1 The structure of Ti–Si–N(O) films deposited at $T = 470$ K and $P(N_2) = 1 \times 10^{-2}$ Pa. Ti$_x$Si$_y$N$_z$(O) phase (B1 structure type): microdiffraction pattern (a) and dark-field electron-microscopy image in (111) and (200) reflections (b).

films. The $Ti_xSi_yN_z(O)$ films were established to have a polycrystalline fine-dispersed microstructure. Dark-field electron-microscopy images show in this case uniformly located coherent scattering regions corresponding to crystallites of about 50 A [Fig. 1(*b*)]. Individual crystallites are of irregular shape with no distinct boundaries. This is characteristic of refractory fine-dispersed materials and stems from the high degree of non-equilibrium in the intergrain boundary structure.

With a decrease and increase in the working nitrogen pressure outside the established range, the film structure becomes biphasic: the cubic phase $Ti_xSi_yN_z(O)$ + an amorphous silicon-containing phase. According to XPS data, at elevated pressures the amorphous phase corresponds to silicon oxynitride. The films obtained at lower nitrogen pressures contain a greater amount of oxygen and the amorphous phase found in these films may correspond to complex titanium- and silicon-based binary oxide whose composition, however, requires more exact definition. An analogous phase was observed with a decrease in substrate potential which is known to lead to a higher oxygen content in the films.[10] The cubic phase lattice parameter varies in the investigated samples from 4.21–4.30 A and depends strongly upon the composition and degree of dispersity of the films. It has been pointed out that the monophase cubic structure extent has its upper limit near the stoichiometric compositions (N/Ti → 1.0); the lower limit is determined by the O/Ti and N/Ti concentration ratio. Therefore, the feasibility of introducing silicon atoms into the nitride (oxynitride) lattice is governed by the stoichiometry degree and the oxygen atom concentration in the non-metallic sublattice.

The influence of substrate temperature on the composition and structure of deposited $Ti_xSi_yN_z(O)$ films has been investigated for a working gas pressure 6×10^{-2} Pa and fixed substrate potential. It was found by XPS that with increasing substrate temperature from 370 to 770 K the nitrogen concentration in the single-phase cubic films rises from 30 to 43 at.%, but those of oxygen and silicon, on the contrary, decrease from 11 down to 7 at.% and from 7 down to tenths of a percent, respectively. At lower deposition temperatures (about 300 K) the film structure becomes biphasic (a cubic phase with crystallite size of maximum 10 A and an amorphous silicon-containing phase), with oxygen and silicon concentrations amounting to 31 and 11 at.%, respectively. Thus, the observed correlation between nitrogen and silicon content in $Ti_xSi_yN_z(O)$ films deposited within the temperature range 370–770 K confirms our conclusions about the effect of the degree of the cubic titanium oxynitride stoichiometry on the introduction of silicon atoms into its lattice.

The regularities observed in the formation of the cubic phase $Ti_xAl_{1-x}N_y$ in ion-plasma vapour deposition make it possible to arrive at the conclusion that the phase $Ti_xAl_{1-x}N_y$ (B1 structure type) is formed both in stoichiometric and superstoichiometric ($y \geqslant 1$) compositions.[11]

The problem of silicon atom localization in the monophase B1 structure of titanium oxynitride has been studied by X-ray photoelectron spectroscopy. Fig. 2 presents XPS Si2p-spectra of the cubic $TiSi_{0.1}N_{0.9}(O)$ film and a profile of silicon distribution over the depth of the film in layer-by-layer ion etching of surface layers. It can be pointed out that: (i) oxidized in air surface layers (to 20 A) are considerably enriched with silicon atoms [Fig. 2(*a*)]; (ii) the XPS Si2p-spectrum on the film surface is represented by two constituents with binding energies of 102.7 and 99.1 eV, respectively; the intensity of the high-energy band decreases with ion etching of surface layers [Fig. 2(*b,c*)].

Analysis of the attested silicon-containing phases has given the following values of binding energy for the Si2p-level: Ti_5Si_3, 98.8 eV; Si, 99.5 eV; Si_3N_4, 101.8 eV; SiO_2, 102.7 eV.

Thus, the constituent of the XPS Si2p-level observed on the film surface at about 102.7 eV corresponds to SiO_2. For silicon atoms in the "bulk" of the $Ti_xSi_yN_z(O)$ film [Fig. 2(*c*)]
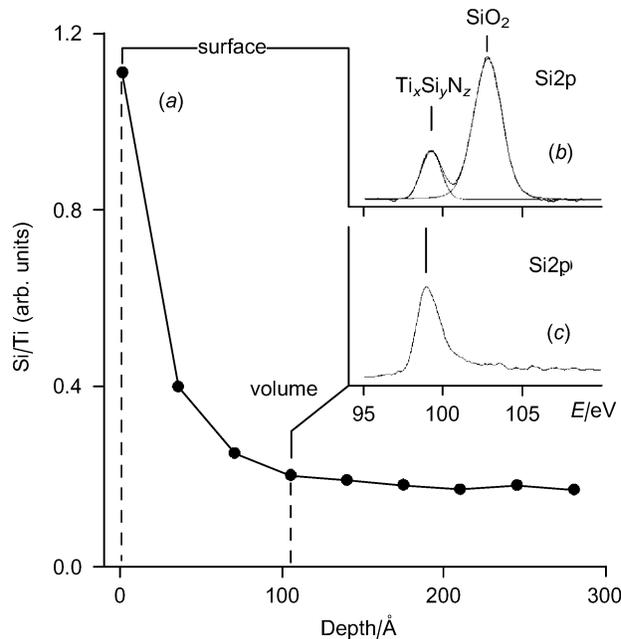

Fig. 2 The profile of silicon atom distribution over the depth of $Ti_xSi_yN_z(O)$ films (*a*); XPS Si2p-spectra on the surface (*b*) and in the "bulk" (*c*) of $Ti_xSi_yN_z(O)$ films.

a chemical shift of Si2p binding energy (99.1 eV) has been established towards lower values relative to metallic silicon (99.5 eV). This fact bears witness to the presence of a negative effective charge on the Si-atoms in $Ti_xSi_yN_z(O)$ and, consequently, to the metallic surrounding of the silicon atoms within the first coordination sphere. The results obtained point unequivocally to the introduction of silicon atoms into the non-metallic sublattice of B1-titanium oxynitride.

We have found a protective surface layer SiO_2 + TiO_2 of a few tens of angstroms to be formed during oxidation in air at room temperature. A similar effect was observed earlier for $Ti_xAl_{1-x}N$ films at considerably higher temperatures.[11]

The possibility of realization of various solid solutions in the Ti–Si–N system (by substituting Ti → Si or N → Si) has been analysed on the basis of self-consistent LMTO calculations[2] of the crystal cohesion energy (E_{coh}) and substitution energy (E_{sub}) for the model systems $Ti_{1-x}Si_xN$ and $TiSi_xN_{1-x}$ ($x = 0.0$; 0.25; 0.50). The results presented in Table 1 indicate that introduction of silicon atoms into the N-sublattice sites is preferable.

Thus, the feasibility of formation of the metastable solid

Table 1 Cohesion energies (E_{coh}/Ry) and substitution energies (E_{sub}/Ry) for cubic silicon-containing solid solutions based on titanium nitride. LMTO-calculations.

Parameter Ry	Compound				
	TiN	$Ti_{0.75}Si_{0.25}N$	$Ti_{0.50}Si_{0.50}N$	$TiSi_{0.25}N_{0.75}$	$TiSi_{0.50}N_{0.50}$

solution film $Ti_xSi_yN_z(O)$ (B1 structure type) has been shown; the range of the monophase structure existence is determined by the degree of stoichiometry (non-metallic sublattice filling) and by the concentration of oxygen in this sublattice. The problem of silicon atom localization in the cubic structure of $Ti_xSi_yN_z(O)$ has been solved both theoretically and experimentally.

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