The Effect of Ion Irradiation on the Composition of Thin TiN, TiAlN, TiAlSiN Films

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Abstract – The structure of nitride covering on the basis of TiN with addition Al and Si was studied by a electron diffraction method before and after an irradiation by Cu and Cr–B ions with energies from 300 (Cu) to 60 keV (Cr–B). It is shown, that a loss of nit6rogen at an ion irradiation leads to occurrence of structural vacancies in TiN lattice. It causes change of structural factors for Bragg's reflections that is shown in occurrence of the forbidden reflexes and intensity change of basic reflexes. Experimental proofs of occurrence of the free titan after ion implantation into TiAlN film are presented.

1. Introduction

Nitride deposition coating TiN, TiAlN, TiAlSiN are used for giving a surface of various metals and ceramics of special properties. TiN (NaCl type lattice) is the base component of such covering. It was shown in a number experiments possibility to modify their service properties by ion implantation of various elements [1–3]. Usually an implantation process is accompanied by dispersion of a target material. In a case of nitride covering the nitrogen atoms may be beaten out by ion irradiation and easily deleted by vacuum system, reducing the nitrogen concentration. If originally the structure of a covering was closed to stehiometric TiN that after an irradiation the part of unit cells in a nitrogen sublattice will appear free, there will be structural vacancies. These changes can be found out by X-ray and electron diffraction methods as occurrence of structural vacancies will change structural factors of the Bragg's diffraction.

2. Structural factors of TiN

In the elementary cell of stehiometric composition TiN titan atoms settle in positions with coordinates 000, 1/2 0 1/2, 0 1/2 1/2, 1/2 1/2 0 and nitrogen atoms in positions 00 1/2, 1/2 00, 0 1/2 0, 1/2 1/2 1/2. The structural factor for reflexes with indexes h, k, l looks like:

$$F_{hkl} = f_{\mathrm{Ti}}\{1 + \cos[-\pi(h + \mathrm{l}) + \cos[-\pi(k + l)] + \\ + \cos[-k\pi(h + k]\} + f_{\mathrm{N}}\{\cos(-\pi l) + \\ + \cos(-\pi h) + \cos(-\pi k) + \cos[-\pi(h + k + l)]\},$$

where f_{Ti} and f_{N} are the atomic factors of scattering for X-ray or electrons. From this expression follows, that for reflexes with even indexes the structural factors are equal:

$$F_{hkl} = 4(f_{\mathrm{Ti}} + f_{\mathrm{N}}),\ (h, k, l \text{ are even}),$$

whereas for reflexes with odd indexes

$$F_{hkl} = 4(f_{\mathrm{Ti}} - f_{\mathrm{N}})),\ (h, k, l \text{ are odd}).$$

Reflexes with the mixed indexes have the structural factor equal to zero that means absence of corresponding reflections. For example, the structural factor for reflex 110:

$$F_{110} = f_{\mathrm{Ti}}(1 - 1 + 1 - 1) + f_{\mathrm{N}}(1 - 1 + 1 - 1) = 0.$$

If any nitrogen atom will replace on vacancy, structural factors will change for all reflections. For reflexes with even indexes they will be equal $4f_{\mathrm{Ti}} + 3f_{\mathrm{N}}$ and for odd indexes they will be equal $4f_{\mathrm{Ti}} - 3f_{\mathrm{N}}$. Reflexes with the mixed indexes will have the nonzero structural factors equal $\pm f_{\mathrm{N}}$. Concurrence of signs on diffraction amplitudes for a greater part of elementary cells in any block of coherent scattering is necessary in this case for reception of appreciable intensity. It is possible if the arrangement of structural vacancies in the block will be ordered. Simultaneously, occurrence of structural vacancies will increase intensity of the reflexes with odd indexes and it will reduce intensity of the reflexes with even indexes. This effect should be considered at the analysis of the structural changes caused by an ion irradiation of TiN and other connections similar to it. X-ray method has been used in recent works [1–3] for studying structural changes after ion implantation of covering on the basis of TiN. It has been established, that intensity of a reflex 200 decreases, and intensity of reflex 111 increases. This result corresponds to the set forth above representation though authors [1–3] give another explanation to this fact. Experimental results of the given work are received by electron diffraction method, allowing investigating structures thin (100–200 nm) surface layers of a coating. This thickness is much less, then it used in X-ray analysis. Therefore, electron diffraction method gives more adequately information about condition of the thin surface layer.

3. Experiment

TiN, TiAlN, and TiAlSiN coverings (thickness t 100–200 nm) were put on NaCl crystals by magnetron methods in the environment of argon and nitrogen a pressure in the chamber which allowed receiving a stehiometric for TiN films. Ion implantation in these films has been executed on the device "Diana". Composite cathode Cr–B was a source of ions with energy 40–60 eV. Irradiation by Cu ions with energy 300–800 eV has been used for substrate clearing before the Cu magnetron deposition on NaCl crystals. TiN reflexes have been found out on electron diffraction patterns (further we shall designate, as EDP) simultaneously with Cu reflections. This effect is caused by the secondary dispersion TiN, covered a sample Table of the device chamber.

The separation of films from substrate was made in the distilled water after end of all operations (including implantation and vacuum annealing). Electronograph ЭМР-102 has been used for making transmitted EDP at an accelerating voltage 100 kV with registration on a photofilm. EDPs were translated in a digital format and then were processed with used of the program Adobe Photoshop CS.

4. Results and discussion

EDP of the Cu + TiN is presented in Fig. 1.

Fig. 1. EDP of Cu + TiN, received after irradiation of substrate by Cu ions with energy 300 eV

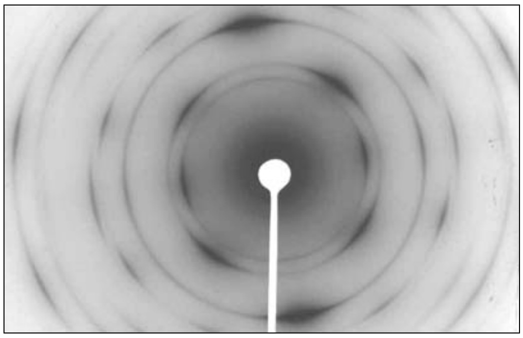
Calculation and decoding of reflexes are resulted in Table 1 (numbering of reflexes is conducting from left to right).

Table 1. Interplane distances *d* and decoding of reflexes for EDP Fig. 1

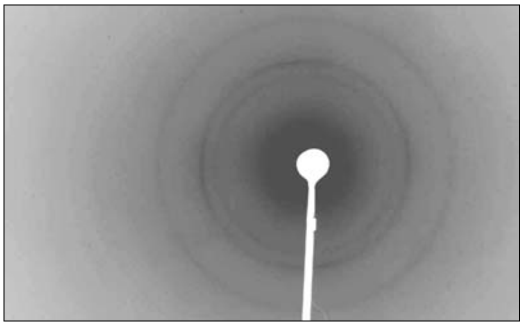
No. refl.	*d*, Å	Decoding
1	3.002	(110) TiN
2	2.452	(111) TiN
3, weak	2.115	(200) TiN
4	2.079	(111) Cu
5	1.801	(200) Cu

There is reflex 110 forbidden for stehiometric TiN. Obvious easing a reflex 200 in comparison with 111, through for stehiometric TiN a parity the return is observed. This result testified to reduction of the maintenance of nitrogen at secondary dispersion TiN by Cu ions. Process of formation of covering is almost equilibrium, therefore it is possible to expect ordering of structural vacancies that gives appreciable intensity of a reflex 110. At Cu ions energies 500 and 800 eV the reflex 110 appears also, but formation of the texture set by a substrate, does less appreciable change of reflexes intensity.

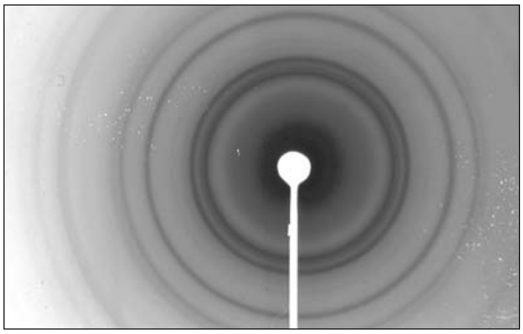
Implantation of Cr–B ions with energies 40–60 eV into TiAlN and TiAlSiN films at fluencies 10^{17} ion/cm^2 and above leads to substantial growth of a EDP background and to easing of reflexes intensity. It is possible to explain this effect crushing of crystal structure with simultaneous formation of an amorphous phase. In this case revealing of weak reflexes is impossible, therefore vacuum annealing at 600 ºC during 30 min has been lead a of the film together with substrate. EDPs of TiAlN coating are presented in Fig. 2 for initial (*a*), implantation by a dose $4 \cdot 10^{17}$ ion/cm^2 (*b*) and after finishing annealing duration of 30 min at 600 ºC (*c*).



a



b



c

Fig. 2. EDP of TiAlN film: *a* – initial condition; *b* – after irradiation by Cr–B ions at fluency $4 \cdot 10^{17}$ ion/cm^2; *c* – after finishing annealing at 600 ºC, 30 min

In initial condition, the coating had the strongly pronounced texture defined by a substrate: the axis of a texture [001] is normal to surface. Implantation has led to essential destruction not only texture, but also a crystal condition in general. Annealing has restored a crystal condition, but not a texture. Obviously, occurrence crystals occurred in an amorphous phase simultaneously on all volume of a film irrespective of a substrate. There is the effect of increasing in intensity of a reflex 111 (the first ring from the center) concerning a reflex 200 (the second ring) in Fig. 2, *c*. A parity the return is observed in initial condition if a texture is absent, differently comparison is complicated. Additional weak reflexes in Fig. 2, *c* have been found out. Interplane distances and decoding are resulted in Table 2 for observable reflexes.

Table 2. Interplane distances *d* and decoding of reflexes for EDP Fig. 2, *c*

No. refl.	*d*, Å	Decoding
1	2.40	(111) TiAlN
2 weak	2.263	(101) α-Ti
3	2.077	(200) TiALN
4	1.47	(220) TiAlN
5 weak	1.748	(102) α-Ti
6 weak	1.351	(103) α-Ti

Weak reflexes in Fig. 2, *c* are related to phase α-Ti, and other reflexes are related to phase TiAlN with lattice parameter 4.16 Å (for pure TiN lattice parameter is equal 4.24 Å). It means, that Al atoms replace of Ti atoms in TiAlN lattice. The size of Al atoms is less, than Ti atoms; therefore, the lattice parameter decreases. Occurrence of the free Ti after annealing is connected with nitrogen deficiency, arisen after ion implantation. Up to annealing the free Ti is not found out, as it is in atomic condition in an amorphous phase.

EDPs of TiAlSiN films are shown in Fig. 3 in an initial condition (*a*), after ion implantation by Cr–B ions with fluency 10^{18} ion/cm^2 (*b*), after final annealing at 500 ºC during 30 min (*c*).

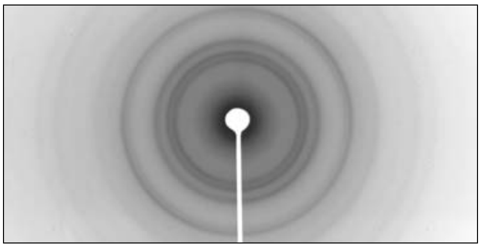
TiAlSiN films have been received by two-magnetron sputtering at one-time work of magnetrons with Ti and Si–Al cathodes.

Interplane distances *d* and decoding for initial condition (Fig. 3, *a*) are resulted in Table 3.

Table 3. Interplane distances *d* and decoding of reflexes for EDP Fig. 3, *a*

No. refl.	*d*, Å	Decoding
1	2.71	(211) TiSi
2	2.408	(111) TiAlN
3	2.085	(200) TiAlN
4	1.557	(411) TiSi
5	1.474	(220) TiAlN

In an initial condition EDP of TiAlSiN shows presence of reflexes TiAlN phase with lattice parameter 4.17 Å and TiSi phase (type *Pnma*). Attributes of a texture is not found out. Ion implantation by Cr–B ions with fluency 10^{18} ion/cm^2 has caused easing reflexes and strengthening of a background (Fig. 3, *b*), that testifies to partial destruction of crystal structure. The subsequent annealing at 400 or 450 ºC during 30 min have lowered a background and have a little increased contrast of reflexes but general character EDP has not changed. More appreciable changes have occurred after annealing at 500 ºC. Initial coating looked like a dark translucent film. Annealing at 500 ºC has made its perfectly transparent. Calculation of EDP Fig. 3, *c* and its decoding are resulted in Table 4.



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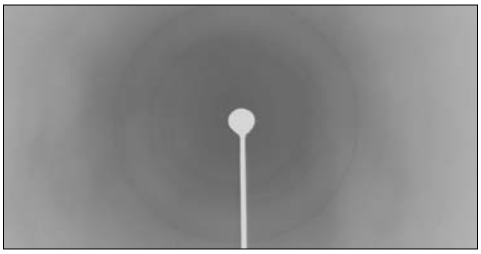
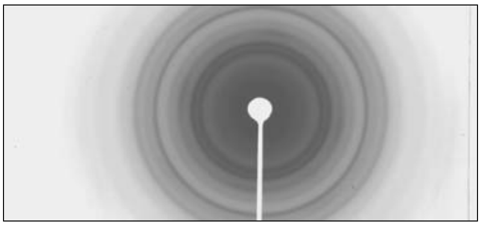


b



c

Fig. 3. EDPs of TiAlSiN films: *a* – initial condition; *b* – after ion irradiation by Cr–B ions; *c* – after final annealing at 500 ºC

Table 4. Interplane distances *d* and decoding of reflexes for EDP Fig. 3, *c*

No. refl.	*d*, Å	Decoding
1	2.74	(111) TiSi
2	2,408	(111) TiAlN
3	2.065	(200) TiAlN
4	1.82	(020) TiSi
5	1,578	(401) TiSi
6	1.452	(220) TiAlN
7	1.336	(321) TiSi

As well as in an initial condition, reflexes of TiAlN and TiSi are observed after annealing only, but their intensity has decreased noticeable. Reflection 200 of TiAlN phase has reduced intensity in comparison with reflection 111, but it necessary to have in view of, positions of a reflex 111 for TiAlN and a reflex 210 for TiSi almost coincide. It is necessary to consider, that reflection 210 for TiSi phase has the greatest intensity, therefore intensity changes of a reflex 111 for TiAlN phase are imperceptible. Possible, free Ti which has formed after implantation, has reacted with the free Si which is available after deposition. Transformation of originally semitrasluchent film in perfectly transparent also is certificate of change its structure aside prevalence TiSi phase, being the semiconductor.

Phases TiN and TiAlN have partially metal properties. Annealing of an initial coating at 500 ºC has not made of appreciable changes.

5. Conclusion

The analysis of structural factors is represented at electron and X-ray investigations for nitride coating on the TiN basis. The occurrence of structural vacancies which is caused by of nitrogen deficiency leads to changes of the basic reflection intensity: it decreases for reflections with even indexes and it increases for reflections with odd indexes. Occurrences of the reflections which are forbidden by structural factor are possible also. Loss of nitrogen atoms occurs at an ion irradiation that proves to be true at electron diffraction research in the present work. Occurrence of the free titan, change of phase balance in TiAlN and TiAlSiN coating after annealing, are consequence of nitrogen deficiency.

References

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