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Formation of (100) texture in thin Ti films under low-energy ion bombardment

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10–40 nm Ti films with mixed crystalline texture (100)+(001) are exposed to ion bombardment in inductively coupled Ar plasma by applying the bias -30 V to the films. It is found that such a treatment leads to the formation of (100) texture in films. This result is explained by the generation of the compressive stress in films as a result of ion bombardment. The thinner the film the less time is required to form the (100) texture.

Keywords: crystalline texture, ion bombardment, titanium, thin films.

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Thin α-Ti films with the (001) texture are used as adhesive underlayers when depositing of ferromagnetic films, TiN, Al, AlN, Pt on various substrates. Strengthening the texture of the Ti underlayer leads to the strengthening the texture and, consequently, to improvement in the performance properties of films and multilayer systems deposited on it [1,2]. In order to change the texture of the Ti films, the parameters of the deposition processes are varied, in particular, ion bombardment of the growing film is used [3,4]. At the same time, the authors did not find any works devoted to the effect of low-energy ion bombardment on the texture of Ti films, after their deposition. Meanwhile, such a procedure can be applied, among other things, to change mechanical stress in metal films [5], and in [6] plasma processing of Ti films was used to prepare the surface of adhesive layers. Purpose of this work is to determine the effect on the texture of Ti thin films of Ar ion bombardment in argon plasma of radio-frequency (RF) inductive discharge.

Ti films 10, 20, 30, and 40 nm thick were deposited on the oxidized Si(100) wafer by magnetron sputtering. The deposition was carried out in Alcatel SCR 651 „Tetra“ setup at room temperature with floating potential on the substrate. The residual pressure was $5 \cdot 10^{-5}$ Pa, the Ar pressure during deposition was 0.2 Pa, the RF power on the target was 300 W, the deposition rate was 20 nm/min, the distance between target and substrate 100 mm. After deposition, the films were kept in air for several days, after which they were subjected to a series of ion-plasma treatments (IPT), which were carried out in radio-frequency inductive discharge reactor in argon plasma, which is described in detail in [7]. During IPT, the Ar pressure in the reactor was 0.08 Pa, the RF power supplied to the inductor was 800 W, the Ar flow rate was 10 sccm, the ion current density was 7.4 mA/cm^2. The films were subjected to a series of four IPTs lasting 30 min each, when RF voltage was applied to the sample holder, as a result of which it acquired the constant negative potential of -30 V. The samples were glued with vacuum grease („High vacuum grease“, Dow Corning) to the holder cooled with helium supplied to the holder, under pressure of 100 Pa; therefore, during IPT, their temperature did not exceed 40°C. The temperature of the samples was measured using an AZ8803 thermometer with a chromel–alumel thermocouple immediately after they were removed from the reactor. Before measurements, the samples subjected to IPT, as well as the original samples, were kept in air for at least a day. Before and after each IPT, θ–2θ diffraction patterns were recorded on DRON-3M diffractometer using CuK_α radiation. The chemical composition of the surface layer for the films was studied using Auger electron spectroscopy (AES) on PHI-660 spectrometer (Perkin-Elmer). The results of AES measurements are presented in the table. It was found that before and after IPT, in a thin (1–2 nm) near-surface layer, in addition to Ti, O is also present, but before IPT, the fraction of O is 45–47 at.%, after IPT, the fraction is O becomes equal to 28–29 at.%, which can be explained

Chemical composition of the near-surface region of Ti films 10 and 20 nm thick: as-deposited and after a series of four ion-plasma treatments (IPTs)

Film	Concentration , at. %			
	C	O	Si	Ti
10 nm (as-deposited)	35	47	–	18
20 nm (as-deposited)	39	45	–	16
10 nm (after IPT)	50	29	9	12
20 nm (after IPT)	50	28	9	13

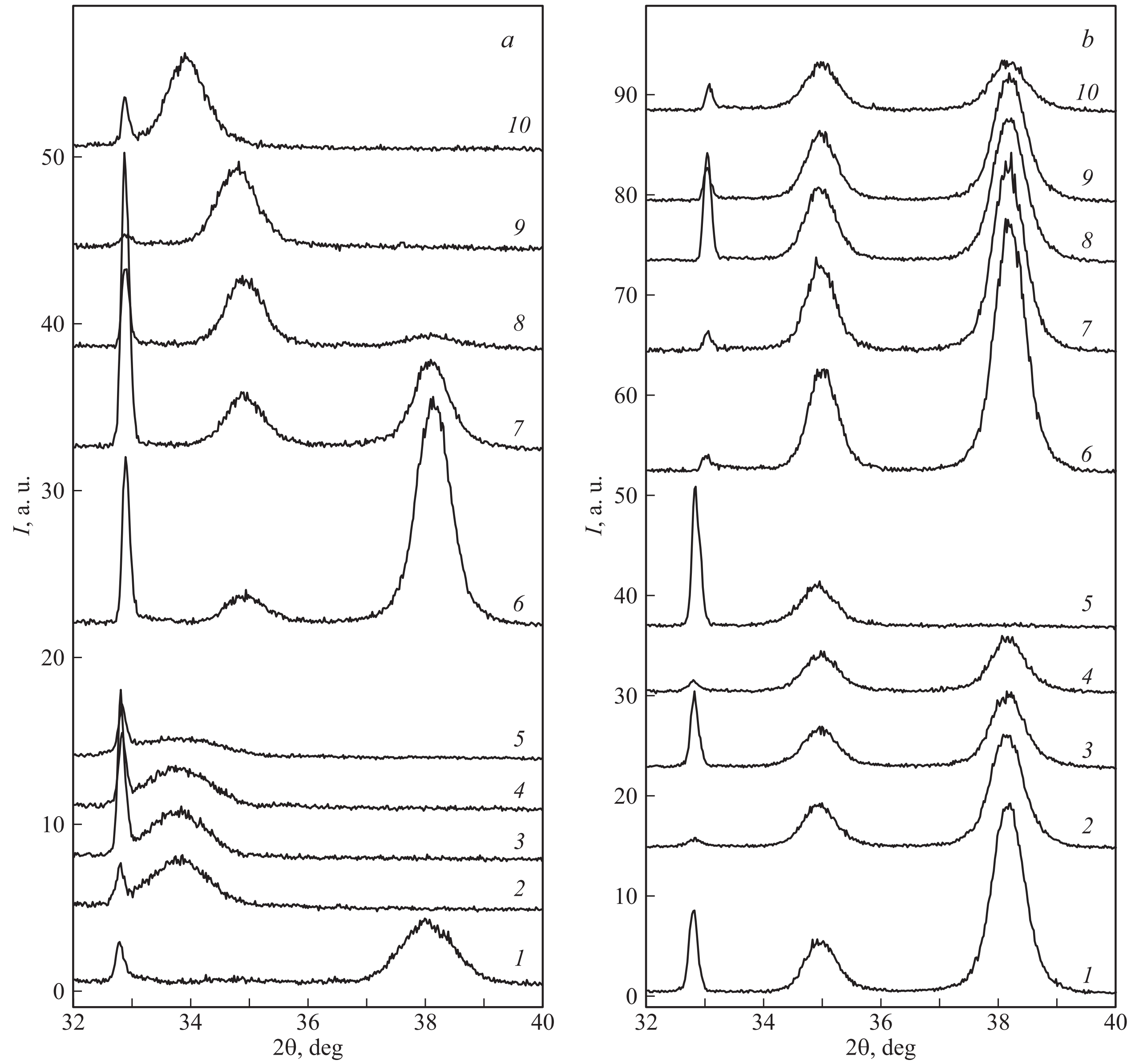

Figure 1. Diffraction patterns of samples with Ti films: for as-deposited films (*1*, *6*) and after one (*2*, *7*), two (*3*, *8*), three (*4*, *9*) and four (*5*, *10*) IPTs. As-deposited film thicknesses: *a* — 10 (*1–5*) and 20 nm (*6–10*); *b* — 30 (*1–5*) and 40 nm (*6–10*). There are observed peaks of Si (200) at $2\theta \sim 33^\circ$, α-Ti (100) at $2\theta \sim 34{-}35^\circ$, α-Ti (002) at $2\theta \sim 38^\circ$.

by the partial removal of oxygen during the sputtering process. The appearance of the Si signal after IPT can be explained by the appearance of pores in the film as a result of sputtering. The film thicknesses before and after IPTs were measured using energy dispersive X-ray spectroscopy (EDS) using an INCAx-act tool (Oxford Instruments) to the Supra-40 scanning electron microscope (Carl Zeiss) according to the method proposed in [8]. It was found that for all samples, as a result of a series of four IPTs, 4–5 nm Ti were removed in total. On the diffraction patterns of the as-deposited and IPT subjected films contains only diffraction peaks at $2\theta \sim 35$ and 38° related to Ti (Fig. 1). The peak at $2\theta \sim 35^\circ$ is the maximum (100) of the α-Ti phase with the hexagonal close-packed lattice. The peak at $2\theta \sim 38^\circ$ is the (002) α-Ti maximum. Its possible identification as the (110) peak of the β-Ti phase with the body-centered cubic lattice is not confirmed by diffraction pattern obtained under tilt angle of 45° sample, which does not show the maximum (200) of the β-Ti phase. Thus, only the α-Ti phase with a (100)+(001) mixed texture is present in all the as-deposited films. It was found that IPTs leads to strong changes in texture: the (002) peak weakens, while the (100) maximum increases. For the film with thickness of 10 nm, already after the first IPT, and for a film with a thickness of 20 nm, after four IPTs, the peak (100) shifts to $2\theta \sim 34^\circ$. No data on Ti phases with such diffraction maximum have been found in the literature. Also, this peak cannot be attributed to the phases of any Ti compounds,

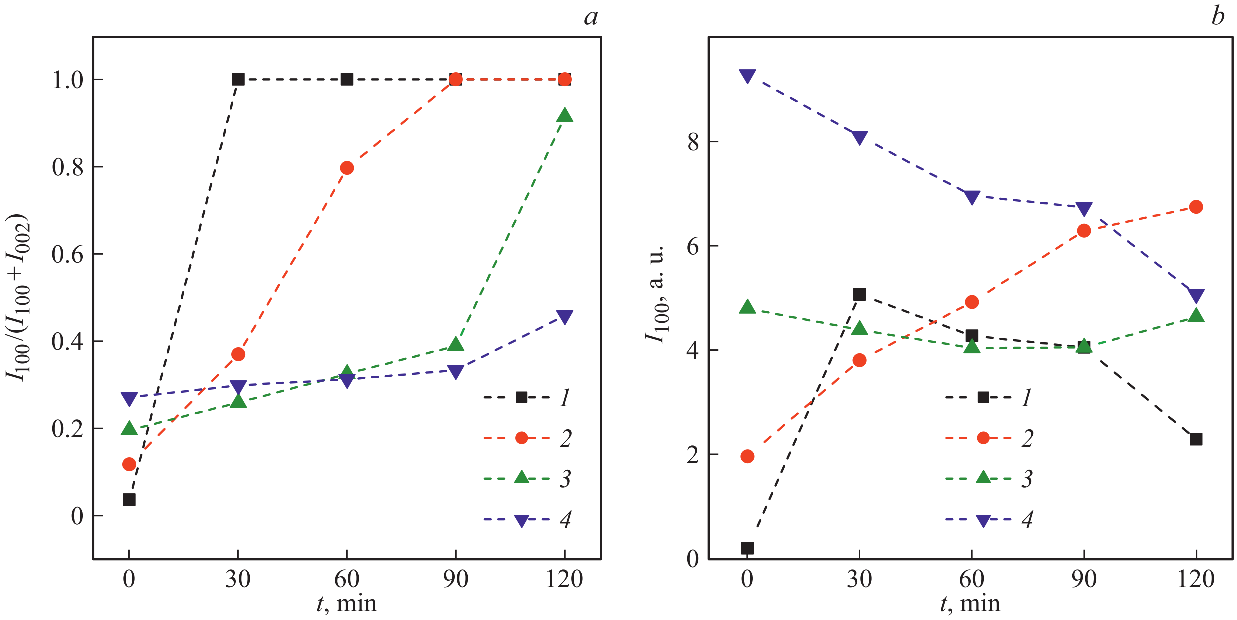

Figure 2. *a* — dependence of the relative peak intensity Ti (100) $I_{100}/(I_{100}+I_{002})$ on the IPT time *t*; *b* — peak intensity Ti (100) I_{100} as a function of IPT time *t*. Ti film thickness, nm: *1* — 10, *2* — 20, *3* — 30, *4* — 40.

since it is absent in the diffraction pattern of a 20 nm thick film after the first three IPTs, while, according to AES, the impurity content in the near-surface region of 10 and 20 nm thick films is before and after the IPT was the same. It can be concluded that the maximum at $2\theta \sim 34^\circ$ belongs to the α-Ti phase.

The dependence of the relative intensity of the (100) peak $I_{100}/(I_{100}+I_{002})$ on the IPT time *t* shows the (001) texture for the as-deposited film 10 nm thick (Fig. 2, *a*). The fraction of (100) oriented grains increases with the increase of the thickness of as-deposited film. It is known that the Ti film with (001) texture has a minimum surface energy [9,10], while the Ti film with (100) texture has a minimum elastic strain energy [3,9,10]. Thus, the increase in the fraction of (100)-oriented grains with increasing film thickness is likely due to an increase in the elastic strain energy. It was found that the number of (100)-oriented grains increases with the IPT time, the faster, the smaller the thickness of the as-deposited film. The increase in the fraction of (100)-oriented grains cannot be explained by the predominant sputtering of (001)-oriented grains. In this case, the intensity of the (100) I_{100} peak would not increase as a result of IPT, however, Fig. 2, *b* shows that in the IPTs series for films with a thickness of 10 nm, I_{100} as-depositedly sharply increases with the IPT time, after which I_{100} weakens, which can be explained by thinning of the film as a result of sputtering. For the film 20 nm thick, there is an increase in I_{100} throughout the series. Since all films are thinned during IPT, the increase in I_{100} for films 10 and 20 nm thick can be explained only by the transformation of (001)-oriented grains into (100)-oriented ones. The intensity I_{100} for the film with thickness of 30 nm varies slightly with increasing *t*, which can be explained by the compensation for thinning of the film by increasing the amount of material in the (100)-oriented grains. In the case of a 40 nm thick film, the increase in the fraction of material with (100) orientation does not compensate for the thinning of the film, so I_{100} decreases with increasing *t*.

It was mentioned above that the (100) texture in α-Ti films is caused by stresses. Based on this fact, one could propose the following qualitative explanation for the reorientation of grains as a result of IPT. In [5,11] it was shown that IPT leads to the increase in compressive stresses in Cr films, which was explained by the diffusion of atoms from the surface into grain boundaries in the framework of the model of the origin of compressive stresses in films proposed in the work [12]. Ion-induced compressive stresses in Ti films can be the driving force that changes the film texture. It is obvious that, the increase in the interplanar distances d_{100} and d_{002} for the (100) and (002) peaks measured in the direction normal to the film indicates the increase in compressive stresses in the film plane. It was found that IPT increases d_{002} and d_{100} in films 10 and 20 nm thick, interplanar distances in films 30 and 40 nm thick vary slightly (Fig. 3). This result generally correlates with the increase in the fraction of (100)-oriented grains.

Ion bombardment promotes an increase in the mobility of adatoms, which in turn increases their diffusion length in the case of surface and grain boundary diffusion. For the same value of the diffusion length of adatoms, the rearrangement of the thinner film obviously occurs faster. The flow of adatoms into grain boundaries will increase with the increasing in the total area of these boundaries. It was found that for the as-deposited samples, the sizes of coherently diffracting domains (CDD), estimated by the Scherrer formula [13], increase with the increasing in the

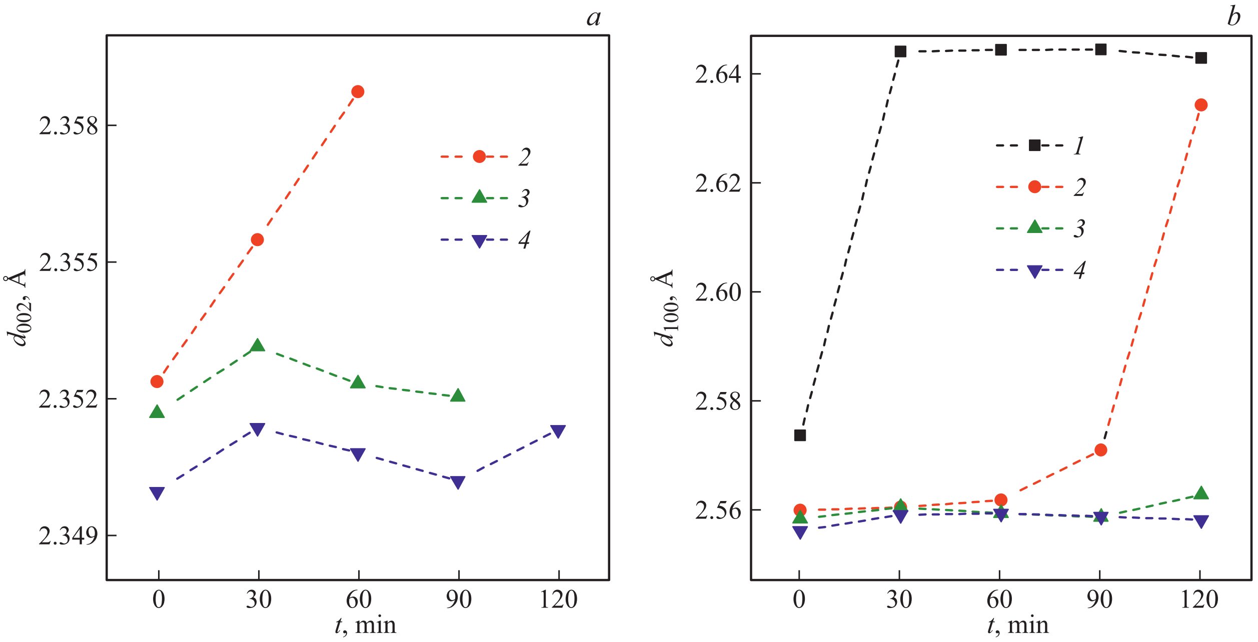

Figure 3. Dependence of the interplanar distances d_{002} (a) and d_{100} (b) in the direction of the normal to the substrate on the IPT time t. Ti film thickness Ti, nm: *1* — 10, *2* — 20, *3* — 30, *4* — 40.

thickness of the as-deposited film from 5–6 nm for a film 10 nm thick to 13–14 nm for a film 40 nm thick. As a result of IPTs series, the CDD decreases by no more than 20%, probably due to thinning of the film. Smaller CDD sizes in the case of the thinner film mean the larger total area of grain boundaries, which in turn means the increase in the atomic flux density during grain boundary diffusion. Significant (3%) increase in the interplanar distance d_{100} for films with a thickness of 10 and 20 nm after IPTs series can be explained by the total effect of a decrease in the size of CDD in nanocrystalline materials as a result of sputtering [14] and increase in compressive stresses.

In [9] the appearance of the (100) texture as a result of the addition of deuterium to the atmosphere during the deposition of Ti by the electron-beam evaporation was explained by such a change in the mobility of adatoms on the (100) and (001) planes due to deuterium adsorption, which made the growth of (100)-oriented grains preferable. In our case, the analysis of the chemical composition of the surface regions of the film indicates the partial removal of oxygen adsorbed on the surface as a result of ion bombardment, as well as the absence of argon after it; therefore, the effect of adsorption of impurities on the rearrangement of grains is not confirmed.

Thus, the work shows that the ion-plasma treatment of thin Ti films leads to a change in texture from mixed (100)+(001) to (100).

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Conflict of interest

The authors declare that they have no conflict of interest.

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