Effect of Implantation of Ba+ Ions on the Composition of MoO_3 Nanofilms Produced by Thermal Oxidation

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Abstract

The determined optimal conditions (oxygen pressure, substrate temperature) for obtaining nanofilms of molybdenum oxides on the Mo(111) surface by the thermal oxidation method. It has been found that the oxidation of Mo(111) with a thin film of Ba ($\Theta \approx 6$ monolayers) oxidizes both Ba and Mo atoms. In the case of Mo(111) implanted with Ba+ ions at a saturation dose (D=6•10-16), Ba atoms are mainly oxidized in the ion-implanted layer. It was also found that in this case, a barrier layer is formed, which sharply hinders (or prevents) the diffusion of oxygen into the depth of the target.

The first found that at T=750-800 K oxide MoO_4 is formed, at T=850-900 K MoO_3, and at T=1000-1200K MoO_2.

Keywords: ion implantation, heating, band gap, barrier layer.

Introduction

Molybdenum oxide nanofilms and multilayer structures based on them are one of the promising materials for modern micro-, nano- and optoelectronics. In particular, thin films of pure and ion-implanted MoO, as well as MoO_3 with a surface film of Ba, Bi, and other metal atoms are widely used in the creation of various solid-state electronic devices [1 – 5].

The physical and chemical properties of Mo O_3 are significantly affected by various external factors (electron and ion bombardment, light irradiation, adsorption and diffusion of foreign atoms and molecules). At present, the effects of temperature [6, 7], ion etching [8, 9], and powerful ion bombardment [10, 11] on metal–insulator phase transitions, magnetic properties and memory switching, and optical and electrical properties of molybdenum oxides are well studied. The composition and electronic properties of Mo implanted with Ba+ ions in an oxygen atmosphere have been studied in the research work [12]. An increase in the coefficient of secondary electron emission by a factor of 3–4 times has been found. Earlier in [13–16], nanosized phases and films of two- and three-component compounds were obtained by implantation of active metal ions on the surface and in the near-surface region of Si, GaAs, CdTe, SiO_2, and CaF_2, and their composition Jand electronic properties were studied. However, studies on the effect of implantation of active metal ions on the physical and other properties of Mo oxides have not yet been carried out.

This research is devoted to studying the composition, crystal structure, electronic and emission properties of MoO_3 implanted with low-energy Ba+ ions in combination with annealing.

Methodology

The target was polycrystalline MoO_3 films with a thickness of ~600 A, obtained by oxidizing single-crystal Mo(111) in an oxygen atmosphere at a temperature of 850 K. Before oxidation, a well-polished single-crystal Mo(111) sample was cleaned under ultrahigh vacuum conditions at T = 1800 K for 20–25 hours and short-term up to T = 2200 K for 10 min. Then oxygen was injected into this device.

Implantation is carried out with Ba+ ions with energies from 0.5 to 5 keV at a saturation dose D = D_{sat} = (6–8) • 1016 cm^{-2}. The barium source is barium titanate (BaTi) tablets. When a quartz tube filled with BaTi tablets is heated, barium vapor is formed, some of which, falling on the surface of a hot tungsten spiral, is ionized. The composition and electronic properties of the surface of materials are studied using the methods of Auger electron spectroscopy (AES) and spectroscopy.

Results and discussion

The following studies were carried out in order to establish the optimal conditions (oxygen pressure, temperature, and heating time) for obtaining MoO_3 nanofilms [16]. First, pure Mo(111) was oxidized at various T for 30 min in an oxygen environment with P_{O_2} =5·10^{-3} Pa (Fig. 1a). Before each oxidation cycle, Mo was degassed at T=1800 for 1 hour at vacuums of ~ 10^{-7} Pa. It can be seen from Fig.1a that Mo is oxidized to the maximum in the temperature range T $\simeq$ 800-1000 K. In the range T=1100-1300 K, Mo is partially oxidized, and at T $\geq$ 1300 K it is practically not oxidized (Fig. 1). Our further studies have shown that in the range T $\simeq$ 500-800 K, peaks characteristic of non-stoichiometric MoO_x oxides (x $\simeq$ 1-4) are found in the Auger spectra of electrons, at T $\simeq$750-800 K, MoO_4 peaks are predominantly detected; K – MoO_3 peaks and at T $\simeq$ 1000-1100 K – MoO_2 peaks.

Fig.1b. shows the change in the intensity of the oxygen Auger peak (E = 506 eV) on the time of Mo oxidation at T = 850 K at various oxygen pressures. It can be seen that at P_{O_2} = 5·10^{-4} Pa, the dependence $I_{auger}(t)$ in the interval t = 0-80 min increases monotonically and almost linearly with increasing t, however, up to t = 120–140 min it does not reach saturation. In the case of P_{O_2} =10^{-2} Pa, the value of I_{auger} (t) up to t$\simeq$ 25 min increases linearly, in the interval t=25-40 min - approximately exponentially, reaching saturation at t $\geq$ 35-40 min. In the case of P_{O_2} = 5·10^{-3} Pa saturation is achieved in time t = 70-80 min.

The AES results measured in combination with the etching of the Mo surface with Ar+ ions showed that the thickness of the MoO_3 film at which saturation is observed is ~ 30-40 Å. It can be assumed that at P_{O_2} =10^{-2}Pa the film growth rate to saturation is ~ 2.5-3 Å/min, at P_{O_2} =5 ·10^{-3} Pa - 1.6-1.8 Å/min, and at P_{O_2} = 10^{-3} Pa - 1-1.2 Å/min.

However, in the case of P_{O_2} = 10^{-2} Pa, the MoO_3 film contained ~5–10 at.% oxides of the MoO_4 type, and in the case of 10^{-3} Pa, the MoO_3 films contained molecules of a nonstoichiometric oxide of the MoO_3–X type.

Their concentration at t = 50 min was ~ 10–15 at.%. The most perfect (homogeneous in depth and surface) MoO_3 films with good stoichiometry were obtained at P_{O_2} ≈5 ·10^{-3} Pa.

Figure 2 shows dependences of O concentration on heating temperature for pure Mo, Mo with a Ba film 6 monolayers thick, and Mo implanted with Ba+ ions with E= 1 keV at D= 6•1016 cm^{-2}.

The heating time at each T is 30 min. In all cases, the oxidation was carried out at T = 850K. it is visible from fig. 2 that in the case of pure Mo (111), the oxygen concentration at T=1000K decreases by 25-30%. Complete removal of oxygen is not observed up to temperatures of 1700–1800 K.

In the case of Mo(111) with a Ba film, both the film (Ba) and the Mo substrates are oxidized. However, Mo is oxidized much less than in the case of pure Mo. At T≃ 850-900 K, the evaporation of the BaO film begins. The film of BaO evaporates completely at a temperature of T≃1100 K. Complete removal of oxygen from the Mo-O composition occurs at T>1600 - 1700 K.

During the oxidation of Mo(111) implanted with Ba+ ions in the near-surface layers, barium is mainly oxidized, while Mo is practically not oxidized. A sharp decrease in the concentration of O begins at T≃ 900-950 K. in the case of ion-implanted samples, there is no noticeable oxidation of Mo.

Figure 3 shows the Auger spectra of pure Mo and Mo subjected to oxidation, previously implanted with Ba ions with E0=0.5 and 1 keV. It can be seen that these spectra mainly contain Auger peaks characteristic of barium oxide, while the intensity of the Mo Auger peaks sharply decrease (or completely disappear). However, their energy positions practically do not change, i.e. Mo practically does not oxidize. This is explained by the fact that during ion implantation, due to the compaction of the near-surface region of Mo, a barrier layer is formed and the diffusion of oxygen deep into the target decreases sharply. Since Mo atoms do not form a chemical bond with barium atoms. It follows from the data presented that the preliminary implantation of Ba+ ions in Mo sharply reduces the oxidation of Mo atoms in the near-surface region of the samples.

Conclusion

It has been established that the most homogeneous $MoO_3/Mo(111)$ nanofilm with good stoichiometry is formed at a substrate temperature of ~ 850-900 K in an oxygen atmosphere with a pressure of ~ P_{O_2} ≈5 ·10^{-3} Pa.

It has been shown for the first time that during the oxidation of the surface of Mo implanted with Ba ions at low energy (E0 = 0.5-1 keV) and at a high dose (D = 6 1016 cm^{-2}), the Ba atoms are mainly oxidized, and the Mo atoms are practically not oxidized, which explained by the high electrical activity of barium. It has been found that the temperatures of complete evaporation of oxygen in the case of Mo-O are ~ 1800 - 1900 K, Ba-O - 1000 - 1100 K.

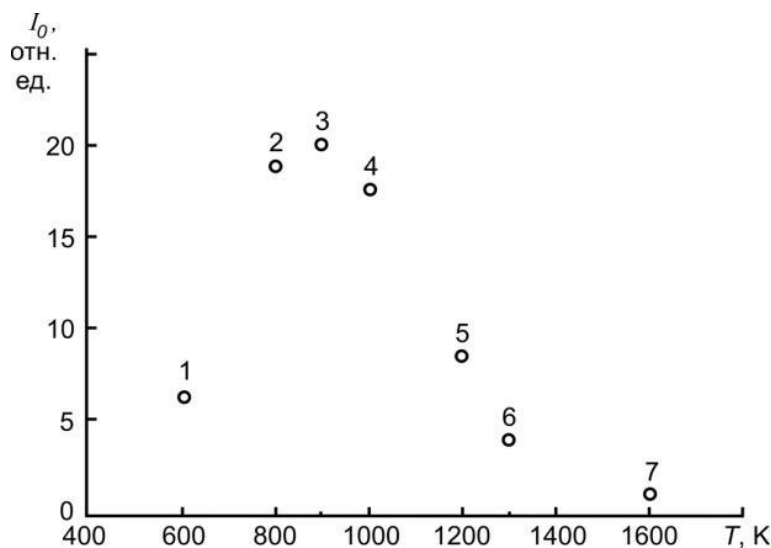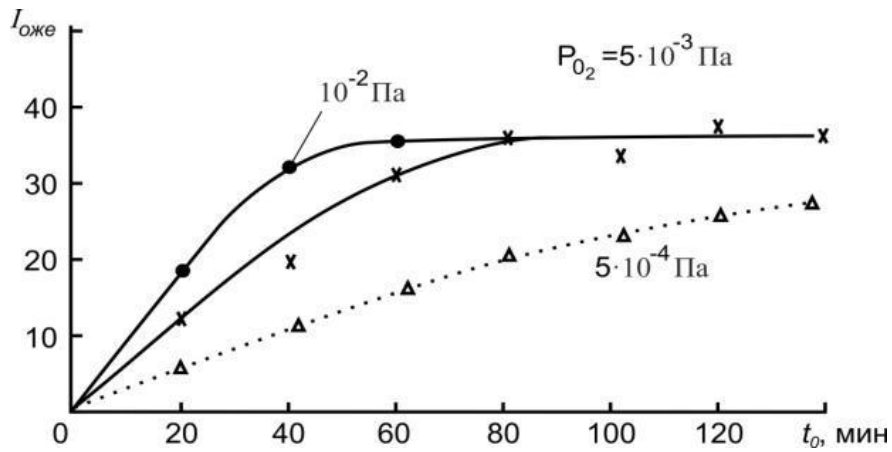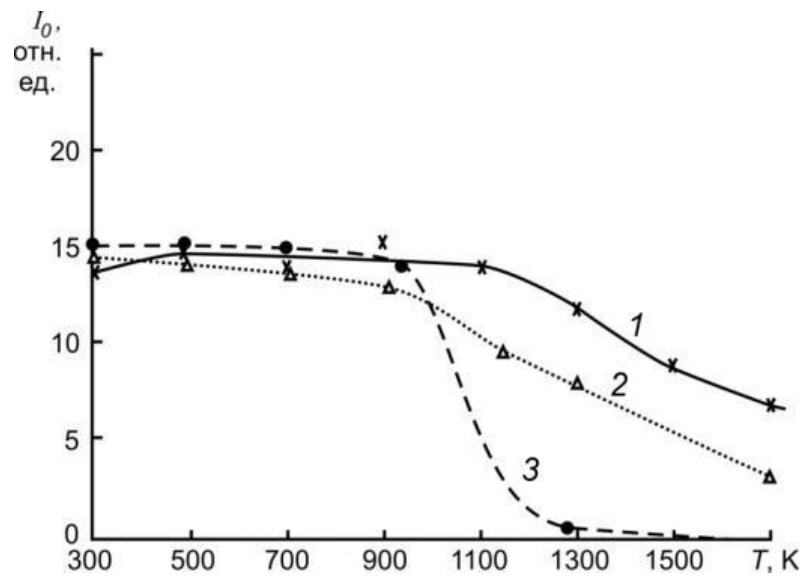**Fig 1a.**

Fig 1b

Fig 2.

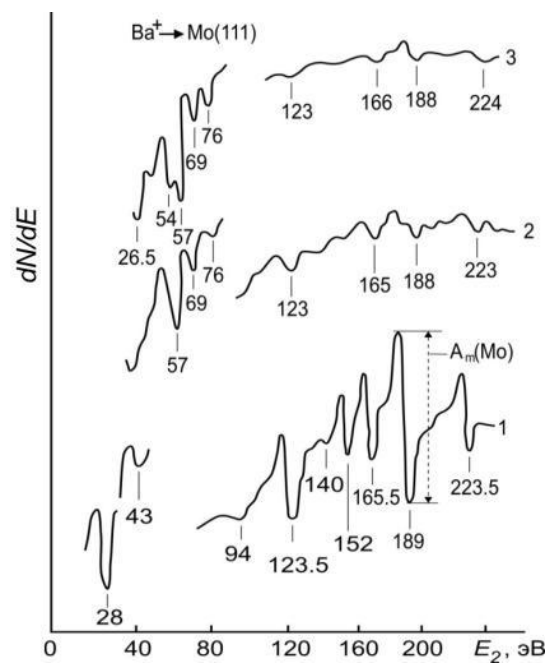**Fig 3.**

Figure captions

Fig 1a. Change in oxygen concentration on the surface of Mo samples when heated in an oxygen atmosphere P_{O_2} =5.10^{-3} Pa

Fig 1b. Dependences of the intensity of the Auger - peak O (E = 506 eV) on the time of Mo oxidation at T = 850 K.

Fig 2. Effect of heating temperature on the surface concentration of oxygen oxidized at T=850 K: 1- pure Mo; 2 - Mo with Ba film with Θ= 6 monolayers, 3 - Mo implanted with Ba+ ions with E0 = 1 keV at D = 6·10^{16} cm^{-2}. Heating at each T was carried out for 30 min.

Fig 3. Auger - spectra of oxidized Mo, previously implanted with Ba ions with E0=0.5 and 1 keV.

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