

FUNCTIONAL COATINGS AND SURFACE TREATMENT

Composition and Morphology of Ti and W Coatings Deposited on Silicon during Ion-Beam Assistance

O. G. Bobrovich^{a*}, O. M. Mikhalkovich^b, and I. S. Tashlykov^{b**}

^aBelarusian State Technological University, Minsk, Belarus

^bBelarusian State Pedagogical University, Minsk, Belarus

* e-mail: olegbobrovich@yandex.ru, physics@bstu.unibel.by

** e-mail: tashl@bspu.unibel.by

Received

Abstract—The composition and structure of Ti and W coatings deposited on (111)Si under ion beam assistance (Ti^+ , W^+) are studied by RBS, TEM, SEM, and SPM. It is found that the structure of the Ti coatings contains a layer of TiSi and $TiSi_2$ silicides and a layer comprising TiC carbides and TiO_2 oxides. The deposition of a W coating results in the formation of a layer containing clusters of W_3Si , W_5Si_3 , and WSi_2 silicides and WO_2 oxide. Ion beam assisted deposition of metal coatings also leads to the amorphization of the surface layer of the silicon substrate. The coating thickness increases with decreasing acceleration voltage for assisting Ti^+ and W^+ ions from 15 to 5 kV.

Keywords: Si, Ti, and W coatings, elemental composition, surface structure

DOI: 10.1134/S207511331503003X

INTRODUCTION

The formation of an interface between the coating and the silicon is an important step in the production of semiconductor devices. In studying the coatings formed by ion beam assisted deposition (IBAD), significant attention is paid to analysis of atomic mixing at the metal/silicon interface, which is caused by the action of accelerated ions of Ar, Kr, and Xe inert gases [1, 2]. Ion irradiation of growing films is used for a controllable variation in some characteristics of thin films and coatings, such as adhesion to the substrate, texture, grain size, and structure, which affect the electrical and optical properties thereof. Disadvantages of the IBAD method include the introduction of inert gases into the surface layer, which can adversely affect the properties and quality of the coating [3].

In our experiments, the deposition of metal coatings was conducted under irradiation assisted with ions of the same metal [4, 5]. Ion bombardment provides the intermixing of the atoms of the metal and the substrate (silicon) at the interface to form new phases, such as silicides [6]. To study these processes, it is necessary to conduct a layer-by-layer elemental analysis and examine the structural phase state and surface morphology of the modified silicon samples.

EXPERIMENTAL

Ti and W metal coatings were deposited on single-crystal (111)Si wafers by bombardment assisted with ions of the deposited metal (Ti^+ , W^+), which were

obtained using a resonance ion source of vacuum arc plasma at an accelerating voltage of 5 and 15 kV [7]. In the case of using electrodes prepared of the material of the deposited coating (Ti, W), the source generates fluxes of ions J_i and neutral atoms J_a of the deposited metal. In our experiments, the ratio of the ion flux density to the neutral atom flux density J_i/J_a was 0.02–0.09; this value corresponded to the growth conditions of the coating on the substrate [8]. At a vacuum chamber pressure of $\sim 10^{-2}$ Pa, the deposition rate of the coatings varied from ~ 0.16 to 0.45 nm/min.

The ion source was also used to prepare two-layer metal/silicon structures during the deposition of neutral metal atoms on a silicon substrate without applying any accelerating voltage for 1 h. After that, coatings with the same composition were deposited on the resulting samples by IBAD.

Layer-by-layer elemental analysis of the initial (111)Si samples, the metal/Si samples, and the samples modified by IBAD of metal coatings was conducted by Rutherford backscattering (RBS) of helium ions with $E_0 = 1.5$ MeV at scattering, entry, and departure angles of 110° , 0° , and 70° , respectively [9], and by computer simulation of the experimental RBS spectra using the RUMP program [10]. The energy resolution of the analysis system was 15 keV, this value provided a depth resolution of ~ 13 nm.

The coating structure was examined by transmission electron microscopy and diffraction using EMV-100A and UEMV-100 instruments. The surface topography of the coatings was studied by scanning electron and

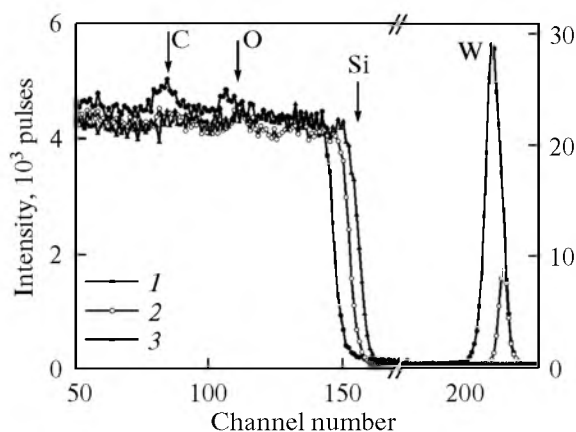


Fig. 1. Experimental RBS spectra of He^+ ions with $E_0 = 1.5$ MeV of the samples: (1) W/Si prepared by IBAD of a W coating at an accelerating voltage of 15 kV, (2) W/Si prepared without ion beam assistance, and (3) initial Si.

scanning probe microscopy using an NT-206 atomic force microscope.

RESULTS AND DISCUSSION

The experimental RBS spectra of He^+ ions of the initial samples and the W/Si samples prepared under proper-ion assisted bombardment and without ion beam assistance are shown in Fig. 1. It is evident that the spectrum of the initial silicon samples does not contain signals of carbon and oxygen impurities; that is, the silicon surface is clean and free from these impurities (or the amount thereof is below the detection limit of the method). The shift of the signal of Si to the region of smaller channels (140–150) in the energy spectra of the modified samples indicates the formation of a coating on the substrate surface; this fact is also confirmed by the appearance of a signal of W in the region of channels 200–250 in the RBS spectra of the coated samples. The peaks in the region of channels 80–110 correspond to the occurrence of carbon and oxygen atoms in the deposited coatings, apparently, from the residual atmosphere of the vacuum chamber of the experimental setup. Qualitatively similar results were observed in the cases of passive deposition (without ion beam assistance) and IBAD of Ti coatings on a Si substrate.

Figure 2 shows the depth distribution profiles of elements in the W/Si samples prepared under different conditions. The position of the interface in the coating/substrate systems was determined using a specially developed technique of introducing a xenon marker [11]. Analysis of the concentration dependences of the distribution of elements in the resulting metal coatings reveals significant differences for different deposited metals and deposition process conditions. At an accelerating voltage of 15 kV, the W atom concentration is 30 and ~40 at % on the surface of the coatings depos-

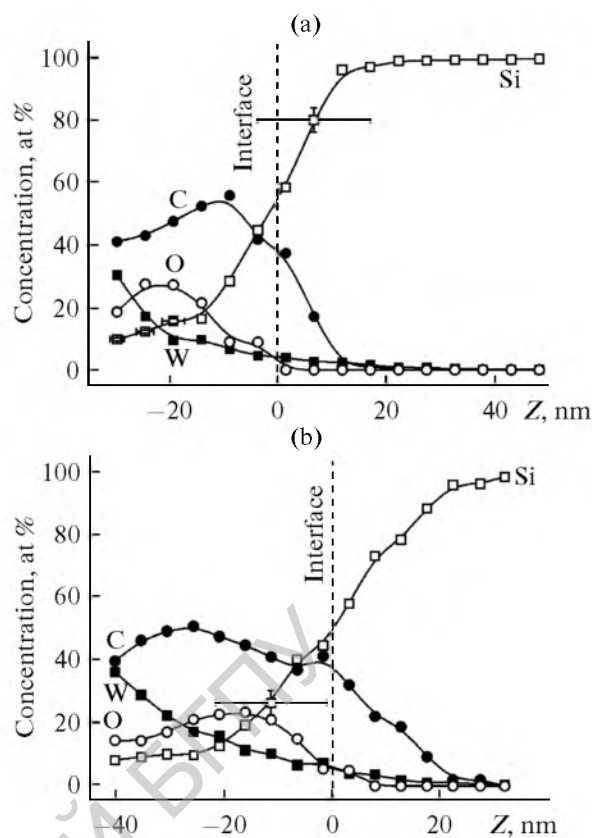


Fig. 2. Depth distribution of elements in the samples with a W coating prepared by IBAD (accelerating voltage of 15 kV) on the samples: (a) initial Si and (b) W/Si prepared by passive deposition of W on Si.

ited on Si and W/Si substrates, respectively. Subsequently, the W concentration gradually decreases to about 2–5 at % at the coating/substrate interface. Deposition of a metal coating on the surface of W pre-deposited on a Si substrate provides the formation of thicker coatings.

The distribution of Ti in the coating exhibits a similar pattern; however, the maximum Ti concentration on the surface is 10 at %; then it gradually decreases to 1.5–2 at % at the coating/substrate interface. A decrease in the accelerating voltage for assisting Ti^+ or W^+ ions to 5 kV makes it possible to increase the thickness of the deposited coatings apparently owing to a decrease in the intensity of dissipation of the deposited layer.

Oxygen and carbon are nonuniformly distributed in the coating. Thus, the oxygen concentration in the coating layer increases to 30 at % and then decreases to 2–5 at % at the coating/substrate interface; in silicon, it becomes lower than the W concentration (Fig. 2a). The distribution of carbon exhibits qualitatively the same pattern; however, the C concentration in the coating is about 2 times higher (~55 at %); at the coating/substrate interface, it decreases to ~40 at %. The carbon content in the Si is an order of magnitude

higher than the W concentration. In addition, the deposited coating contains 10–40 at % Si throughout the entire thickness; the appearance of the silicon is attributed to counterdiffusion from the substrate. A similar effect of counterdiffusion of sulfur on the surface from the bulk of IBAD-modified rubber was previously observed in the case of deposition of metal coatings on an elastomer [12].

Atomic force microscopy has revealed that the surface roughness of the initial Si does not exceed 0.2 nm and increases to 1.1 nm after deposition of Ti coatings (Fig. 3).

Figure 4 shows results of electron microscopic studies of the structure and phase composition of the surface layers of Si. The data suggest that IBAD improves the efficiency of formation of metal coatings on (111)Si wafers. The resulting films have a fairly homogeneous composition over both the surface and the thickness of the sample. Compared to the passive deposition of metals, the formation of a thicker modified surface layer was registered in all cases of IBAD; this fact can be attributed to the ion-stimulated formation of phases (metal silicides, oxide and carbide phases).

In the event of IBAD, an effect of the mass of the assisting ions is observed. Irradiation with heavier ions (W^+) leads to the formation of a thin continuous amorphous layer on the surface of Si wafers. The diffraction patterns of these samples contain, along with matrix reflections, diffuse rings, which indicate the disordering of the material (Fig. 4a). Ti^+ ion bombardment also leads to the amorphization of the surface layers; however, in this case, these layers are located at a greater distance from the surface and commonly are not continuous on the surface (Fig. 4c).

In the case of deposition of thin coatings without accelerated ion assistance, the formation of any phases containing Si atoms was not detected. However, the deposited Ti layers contain oxides and carbides; this fact can be attributed to both a high chemical activity of Ti and the presence of residual gases in the vacuum chamber. The processes occurring during IBAD of Ti significantly inhibit the formation of oxide and carbide phases; this feature can be associated with the destructive effect of the bombarding ions on the resulting oxide and carbide phases and the stimulation of the formation of silicides. It was found that the coating formed by IBAD of Ti comprises two layers (Fig. 5a): a layer of $TiSi$ and $TiSi_2$ silicides with a grain size of about 50–100 nm located on the Si substrate (layer 2) and a thin layer of TiC carbides and TiO_2 oxides with a grain size of about 10–30 nm formed on the surface of the silicide layer (layer 1). Free titanium was also found in the composition of the coating.

The structure of the W coating prepared by IBAD comprises regions with a size of about 5–10 nm that contain clusters of tungsten silicides (W_3Si , W_5Si_3 , WSi_2) and oxides (WO_2) (Fig. 5b). The diffraction pattern also exhibits amorphous rings characteristic of both tungsten silicides and oxides.

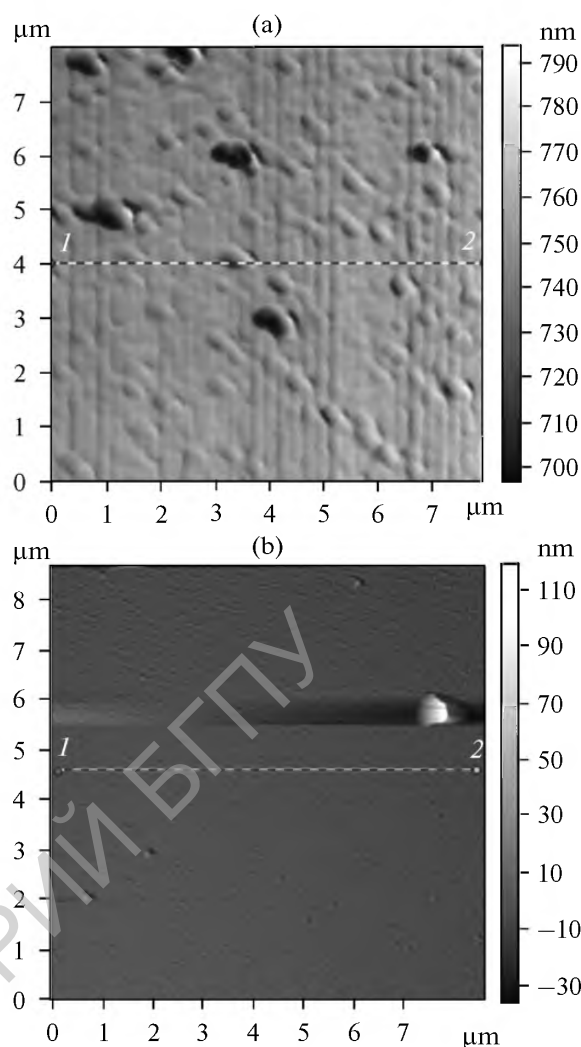


Fig. 3. Surface topography of the samples: (a) initial Si and (b) Ti/Si prepared by IBAD.

In addition to the formation of silicides, carbides, and oxides, the amorphization of the surface layer of the Si substrate is observed in the case of IBAD of metal coatings.

CONCLUSIONS

It has been found that the composition of the metal coatings prepared by IBAD of Ti or W on the surface of a (111)Si substrate contains process impurities C and O, which are present in the residual atmosphere of the vacuum chamber, and Si, which penetrates into the coating owing to counterdiffusion from the substrate.

With a decrease in the accelerating voltage for assisting W^+ ions from 15 to 5 kV, the thickness of the W coating increases from about 30–45 to about 90–120 nm; this fact is attributed to a decrease in the intensity of surface dissipation.

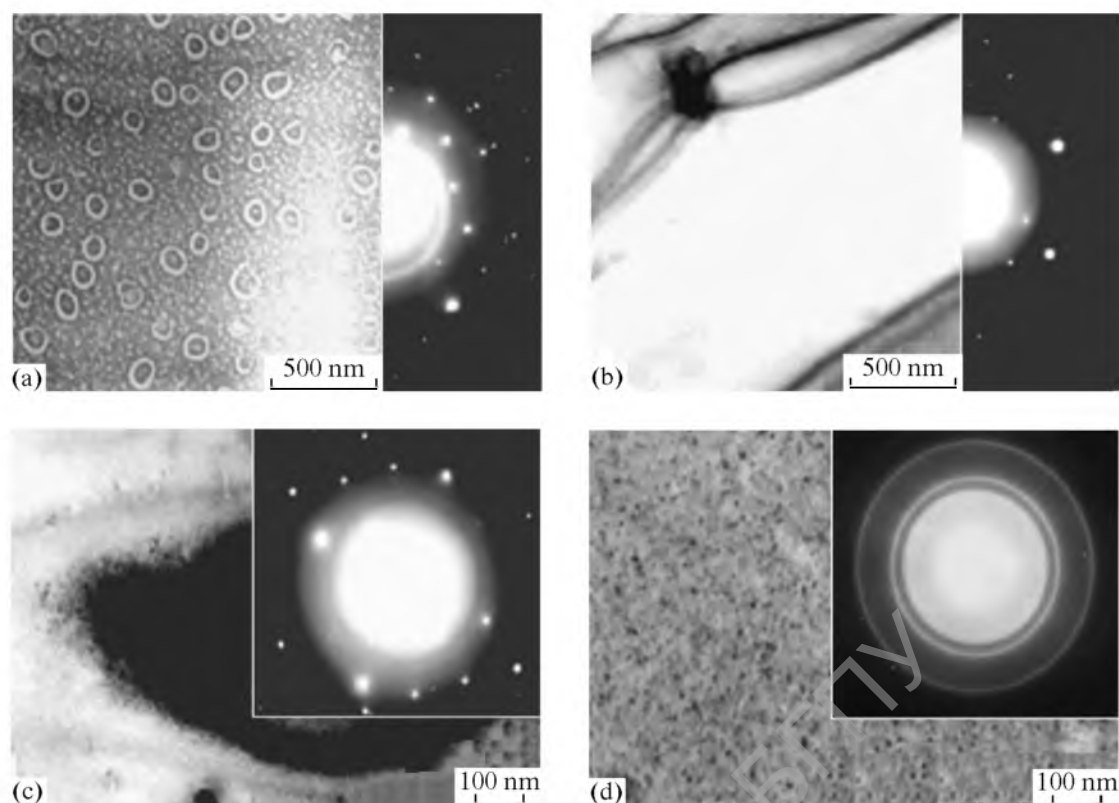


Fig. 4. TEM images of the structure and respective diffraction patterns of (a, b) W and (c, d) Ti coating prepared by IBAD on the samples: (a) W/Si prepared by passive deposition of W on Si, (b) initial Si, (c) Ti/Si prepared by passive deposition of Ti on Si, and (d) initial Si.

The deposited Ti coating comprises two layers with different structures: a layer containing TiSi and TiSi₂ silicides with a size of about 50–100 nm, which is located on the substrate, and a layer containing TiC carbides and TiO₂ oxides with a size of about 10–30 nm, which is located above the former layer. Free titanium is also found in the coating. The deposition of W coatings leads to the formation of a single layer on the substrate; it contains regions of clusters of W₃Si, W₅Si₃,

and WSi₂ silicides and the WO₂ oxide with a size of about 5–10 nm.

IBAD of metal coatings on Si samples with a layer of the same metal predeposited without ion beam assistance provides the formation of thicker coating films containing silicides of these metals.

In addition to the formation of silicides, carbides, and oxides, the amorphization of the surface layer of the Si substrate is observed in the case of IBAD of metal coatings. Bombardment with heavier assisting W⁺ ions leads to the formation of a thin continuous amorphous layer on the surface of Si wafers. Bombardment with assisting Ti⁺ ions also results in the formation of amorphous layers in the surface region of Si; however, these layers are located at a greater distance from the surface and commonly are not continuous on the surface.

The surface roughness of the Ti/Si and W/Si samples prepared by IBAD of metal coatings remains low; this fact suggests that the surface is of high quality and meets the requirements for microelectronic products.

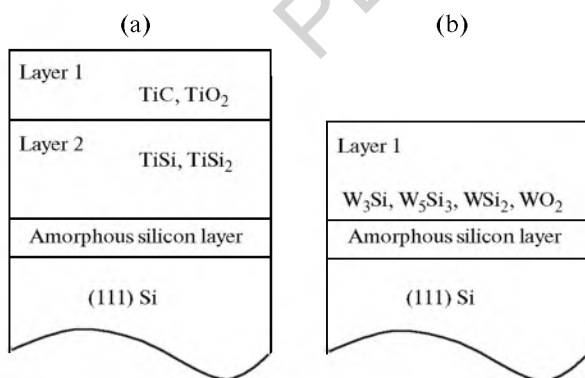


Fig. 5. Structural diagram of (a) Ti and (b) W coating prepared by IBAD on (111)Si.

REFERENCES

1. Gotoh, Y., Nagao, M., and Ura, T., Ion beam assisted deposition of niobium nitride thin films for vacuum

- microelectronics devices, *Nucl. Instrum. Meth. Phys. Res.*, 1999, vol. 148, pp. 925–929.
2. Carter, G., Colligon, J., and Tashlykov, I.S., A simple theory and experimental investigation of ion assisted deposition of cobalt on silicon, *J. Adv. Mater.*, 1999, vol. 5, pp. 1–6.
 3. Mohan, S. and Krishna, M.G., A review of ion beam assisted deposition of optical thin films, *Vacuum*, 1995, vol. 46, pp. 645–659.
 4. Tashlykov, I.S., Bobrovich, O.G., and Baraishuk, S.M., Composition and damage of silicon surface at ion assisted deposition of thin films, *Poverkh. Rentgen., Sinkhrotr. Neitron. Issled.*, 2009, no. 5, pp. 92–95.
 5. Tul'ev, V.V. and Tashlykov, I.S., Study of composition content of Cr, Ti and Zr-based coatings, formed on aluminum and silicon in conditions of self-radiation, *Proc. 4th Int. Conf. "Radiation and Heat Effects and Processes in Inorganic Materials"*, Tomsk., 2004, Surzhikov, A.P., Ed., Tomsk: Tomsk. Politekhn. Univ., 2004.
 6. Hirvonen, J.K., Ion beam assisted thin film deposition: Fundamentals and applications of IBAD processing, in *Materials and Processes for Surface and Interface Engineering*, Pauleau, Y., Ed., Netherlands: Kluwer Academic, 1995, pp. 307–346.
 7. Belyi, I.M. and Tashlykov, I.S., RF Patent 2324, *Byull. Izobret.*, 1999, no. 1, p. 30.
 8. Bobrovich, O.G. and Tashlykov, I.S., Metal-containing coating formation on graphite in the conditions of ion assistance, *Mater. 5 mezhdunar. konf. "Vzaimodeistvie izlucheniya s tverdym telom"* (Proc. 5th Int. Conf. "Interaction of Radiations with Solid", Minsk, 2003).
 9. Komarov, F.F., Kumakhov, M.A., and Tashlykov, I.S., *Nerazrushayushchii analiz poverkhnosti tverdykh tel ionnymi puchkami* (Non-destructing Analysis of Surfaces of Solids by Ionic Beams), Minsk: Universitetskoe, 1987.
 10. Doolittle, L.R., A semiautomatic algorithm for Rutherford backscattering analysis, *Nucl. Instrum. Meth. Phys. Res.*, 1986, vol. 15, pp. 227–234.
 11. Bobrovich, O.G., Tashlykov, I.S., and Glukhatarenko, T.I., Study of phase interfaces in Ti–Si structure with using of Xe marker, *Trudy Bel. Gos. Tekhn. Univ., Ser. 6. Fiz.-Matem. Nauki i Inform.*, 2005, no. 13, pp. 90–92.
 12. Tul'ev, V.V., Veres, O.G., and Tashlykov, I.S., Study of structure and chemical joints in W-based coatings, obtained on elastometer by ion—assisted deposition method, *Mater. 7 mezhdunar. konf. "Vzaimodeistvie izlucheniya s tverdym telom"*, Minsk, 2007 (Proc. 7th Int. Conf. "Interaction of Radiations with Solid", Minsk, 2003).

Translated by M. Timoshinina

SPELL: 1. OK