

Structure and morphology of nano-sized W–Ti/Si thin films

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Abstract: Thin films were deposited by d.c. sputtering onto a silicon substrate. The influence of the W–Ti thin film thickness to its structural and morphological characteristics of a nano-scale were studied. The phase composition and grain size were studied by X-ray diffraction (XRD), while the surface morphology and surface roughness were determined by scanning tunneling microscopy (STM). The analysis of the phase composition show that the thin films had a polycrystalline structure – they were composed of a b.c.c. W phase with the presence of a h.c.p. Ti phase. The XRD peak in the scattering angle interval of 38°–43° was interpreted as an overlap of peaks corresponding to the W(110) and Ti(101) planes. The grain size and the mean surface roughness both increase with the thickness of the thin film. The chemical composition of the thin film surface was also analysed by low energy ions scattering (LEIS). The results show the surface segregation of titanium, as well as a substantial presence of oxygen on the surface.

Keywords: PVD W–Ti thin film, scanning tunnelling microscopy (STM), low energy ions scattering (LEIS), X-ray diffraction (XRD).

INTRODUCTION

Tungsten – titanium (W–Ti) thin films were developed as an alternative to titanium-based films, which were considered as protective coatings.¹ Thin films of W–Ti with specific structural and other properties can be used in very important fields: protective materials – anticorrosion and oxidation resistant films, micro-electronics – diffusion barriers, and gas sensors for the detection of pollutants such as CO, NO₂ and SO₂.^{2,3} In addition to high hardness and adhesion, these films should be thermally stable and oxidation resistant.⁴ Modifications of the microstructure in the presence of the active element (titanium) in W–Ti alloys can influence diffusion rates and mechanical properties of the thin films, playing an important role in the oxidation behaviour of the material.¹

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To improve the characteristics of a tungsten thin film used as a gas sensor and diffusion barrier, Ti atoms were added to W, using a $W_{0.9}Ti_{0.1}$ (w.t.) metallic target for the sputtering process. Investigation of the structural and morphological characteristics on a nano-scale is important for the practical applications of these films. Overlapping of peaks attributed to W and Ti phases occurs in the X-ray diffraction (XRD) analysis of W–Ti thin films.⁵ The deconvolution of the resulting peak at $2\theta = 40^\circ 20'$ yielded an identification of the b.c.c. W(110) and h.c.p. Ti(101) phases.

In this work, the structural and morphological characteristics of W–Ti thin films sputter deposited on single crystal Si(100) *vs.* the film thickness over a wide range from 10 nm to 900 nm were investigated. The grain size and the surface roughness on the nano-scale were measured and analysed. The surface composition was also determined using low energy ion scattering (LEIS).

EXPERIMENTAL

Thin film deposition

The tungsten – titanium thin films were deposited by d.c. sputtering of a sintered target (90 % W – 10 % Ti w.t.) by Ar^+ ions. The substrate used in the experiment was single crystal silicon(100). The standard procedure was applied for preparing the substrates prior to film deposition – the substrates were cleaned in HF solution and deionised water. The deposition was performed at room temperature using a Blazers Sputtron II vacuum system. The acceleration voltage ($U = 1.5$ kV) and current on the target ($I = 0.7$ A) were maintained constant during the experiment. The base pressure in the chamber was $p = 1.33 \times 10^{-3}$ Pa and the partial pressure of argon was $p_{Ar} = 1.33 \times 10^{-1}$ Pa. Under such conditions, the constant deposition rate was 0.095 nm s^{-1} . After deposition, the thickness was measured by a profilometer – Talystep I. The thicknesses of the W – Ti thin films ranged from 10 nm to 900 nm.

Phase composition of the thin films

The phase composition and crystalline structure of the W–Ti deposits were determined by the X-ray diffraction method using a SIEMENS diffractometer with $CuK\alpha$ radiation. The powder X-ray diffractograms were obtained with Ni filtered emission. Angles 2θ in the range from 30° to 80° were scanned in steps of 0.02° in a time sequence of 1 s. Phase identification was made by comparing the diffraction patterns with Joint Committee on Powder Diffraction Standards cards.⁶

Crystalline sizes (D) were determined by applying the corrected Scherrer equation (1):

$$D = \frac{a\lambda 360 \times 10^{-10} m}{2\pi\beta \cos\theta} = \frac{79.5 \times 10^{-10} m}{\beta \cos\theta} \quad (1)$$

where: a is a geometrical coefficient ($a = 0.9$ for cubic crystals), λ is the wavelength of the X-ray beam ($\lambda_{CuK\alpha} = 1.5418 \times 10^{-10}$ m), 2θ is the reflex from the reference sample (crystalline size larger than 500 nm), $\beta = \sqrt{b^2 - B^2}$ is the corrected line broadening, B is FWHM of the peak and b is a correction factor.⁷ The FWHM values were determined using a Gaussian fit and $K\alpha$ -stripping with freeware evaluation software (Diffract Plus – BRUNER - axs).

Surface morphology of the thin films

The surface morphology and surface roughness of the deposited W–Ti thin films were analysed by scanning tunnelling microscopy (STM) Nanoscope III at room temperature under atmospheric pressure. The STM images were obtained in the constant current mode using a Pt(10 %Ir) tunnelling tip. The surface roughness of the deposited W–Ti polycrystalline thin films was measured using the section analysis program in the frame of the STM software.

Chemical composition of the film surface

Low energy ions scattering (LEIS) experiments were performed using the setup described in detail elsewhere.⁸ Ions of Ne^+ in the energy range 1–2 keV were scattered from a W-Ti sample placed in the UHV chamber. The incoming angle φ and the scattering angle θ can be continuously changed in the range 0° to 90° . This range of incoming and scattering angles also provides for analysis by direct recoil spectrometry (DRS). The typical ion current density during the measurements was about $1 \mu\text{A}/\text{cm}^2$. During the experiment, the pressure in the chamber was lower than 5×10^{-9} mbar. The sample was cleaned by grazing incidence sputtering with Ar^+ ions until the steady state was obtained.

RESULTS AND DISCUSSION

The XRD diffractograms of the W-Ti thin films deposited on a silicon substrate with three different thicknesses (10, 150 and 440 nm), are presented in Fig. 1(a–c). For very thin tungsten – titanium films (10 nm), a single peak in the range of $65 - 74^\circ$ (denoted here as peak A) of relatively low intensity can be observed. Two peaks are present in the XRD spectrum of the 150 nm thick W-Ti film: In addition to the previously mentioned peak A, an additional peak appeared in the range of $38 - 43^\circ$ (denoted here as peak B). Finally, only peak B was present in the XRD spectrum of the 440 nm thick W-Ti film sample. Peak A is attributed to the reflection from the Si(400) plane, at the position $2\theta = 69.103^\circ$ according to the JCPDS card (35-1241). This interpretation was confirmed by measuring the XRD spectrum of the Si(100) substrate for the same scattering geometry. Peak B consists of two overlapping peaks corresponding to W(110) at $2\theta = 40.264^\circ$ (JCPDS card 04-0806) and Ti(101) at $2\theta = 40.170^\circ$ (JCPDS card 44-1294). The position of the

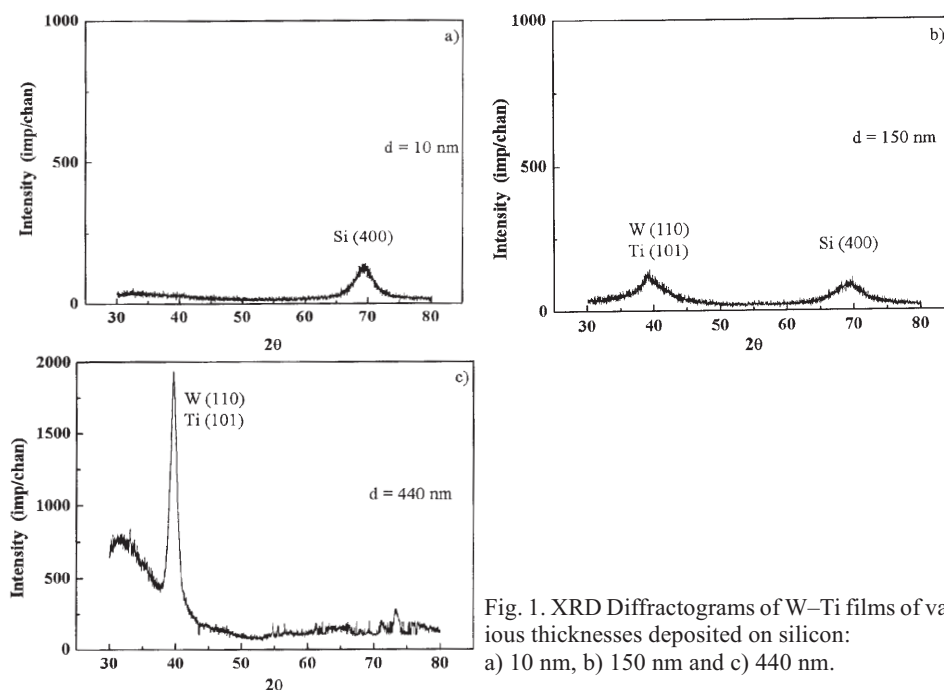


Fig. 1. XRD Diffractograms of W-Ti films of various thicknesses deposited on silicon: a) 10 nm, b) 150 nm and c) 440 nm.

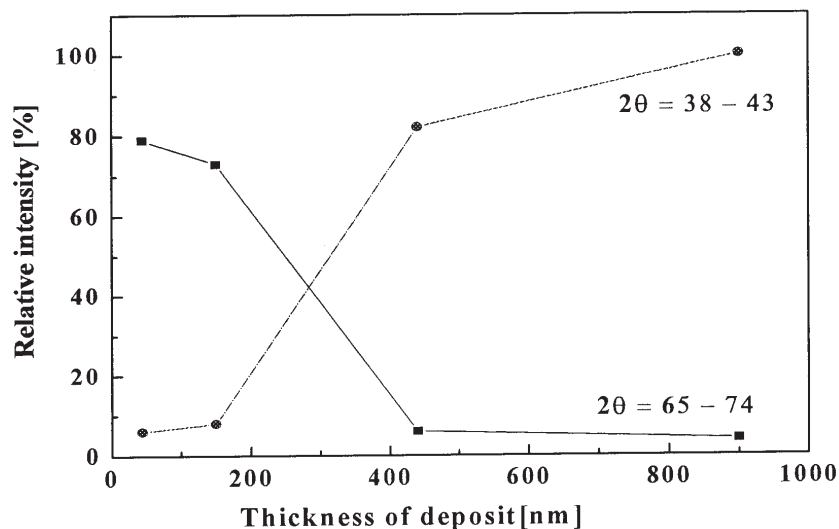


Fig. 2. Intensity of XRD peaks at $2\theta = 38 - 43^\circ$ and $2\theta = 65 - 74^\circ$ as a function of thicknesses of W-Ti deposited on Si.

mentioned peak coincide well with the center of the interval $2\theta = 38 - 43^\circ$ at which peak B is situated. Moreover, they are the most intensive peaks in the XRD spectra of the corresponding reference samples. This interpretation agrees with that of other authors:⁵ polycrystalline W-Ti thin films are composed of a body centred cubic W phase (S.G.: Im3m(229)), accompanied by a hexagonal closely packed Ti phase (S.G.: P6₃/mmc(194)).

The peak intensities vs. the thin film thickness are presented in Fig. 2. It is clear that intensity of peak A decreased with increasing thin film thickness and practically vanished between 150 and 440 nm. This behaviour can easily be explained knowing that this peak corresponds to the substrate: the intensity of peak A decreased with film thickness due to the limited information depth of the XRD technique. The dependence of the intensity of peak B, which corresponds to the thin film itself, can also be explained by its origin. The absence of peak B at 10 nm is partly due to the low surface sensitivity of the XRD technique, and certainly due to the very small size of the crystalline grains. Consequently, the peak grows with increasing film thickness and also becomes narrower (*cf.* Fig. 1) due to the increase of the grain size. According to the original composition of the target (W_{0.9}-Ti_{0.1} w.t.) used for the deposition of the W-Ti thin films, it can be assumed that the dominant phase is b.c.c. W with the texture in the (110) direction.

As an example of the LEIS results, two spectra on Ne⁺ ions scattered from W-Ti surface are presented in Fig. 3. The energies of the primary ions were 1 keV and 2 keV. The incoming and scattering angles were 20° and 40°, respectively. Three peaks, corresponding to oxygen, titanium and tungsten, are clearly visible. In the case of spectra obtained with 1 keV ions, a peak that corresponds to directly recoiled (DR) oxygen

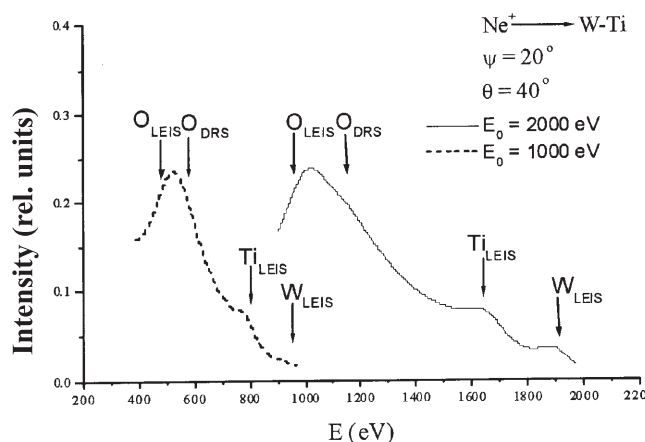


Fig. 3. Energy distributions of Ne^+ ions scattered from W-Ti surface.

ions is also observed. The broad maximum in the spectrum of the 2 keV ions is superimposed from LEIS and DR peaks corresponding to oxygen. The very pronounced oxygen signal in spite of the high neutralization probability and low scattering cross-section can only be due to its domination in the first atomic layer. The peak attributed to Ti appears in both spectra while the tungsten peak is clearly visible only for primary ion energies of 2 keV, when the information depth is greater. This implies that tungsten is not present in the first atomic layer. The absence of tungsten at the W-Ti thin film surface cannot be explained by standard alloy segregation models.^{9,10} Hence, it is most probably related to the increased surface concentration of oxygen: according to the thermodynamical consideration of the most stable tungsten and titanium oxides (WO_3 *i.e.*, TiO_2), the formation of TiO_2 ($\Delta H_{\text{form}} = -944$ kJ/mol) is energetically favoured over the formation of WO_3 ($\Delta H_{\text{form}} = -841.3$ kJ/mol). The presence of oxygen at the surface during the LEIS experiments can be explained by the exposure of the thin film to the atmosphere before the measurements. The presented assumptions for different film thicknesses are confirmed by additional LEIS and X-ray Photoelectron Spectroscopy (XPS) measurements.¹²

The grain size dependence on the deposit thickness is presented in Fig. 4. For a deposit thickness of 100 nm, the grain size is 7.1 nm. The grain size increases up to 13.7 nm for a thickness of 150 nm, probably due to the association of two grains. For greater thicknesses (up to 900 nm), the grain size increases monotonously to about 31 nm, for the highest thickness. However, it does not change significantly in the range from 440 nm to 900 nm: it appears that the grain size reaches its saturation value for thicknesses greater than 440 nm.

The results of the STM analysis showed that the resolution and the vibration stability of the instrument were good enough to obtain reproducible image, revealing details of the surface morphology of the sputtered W-Ti thin films. The surface morphologies of the deposited films are presented in Fig. 5 (a-b). The STM micrographs indicate that the deposited films have polycrystalline forms with a fine

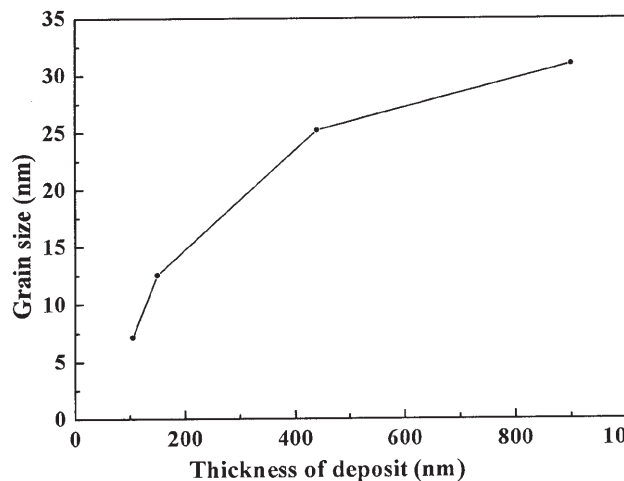


Fig. 4. Grain size of W-Ti thin films as a function of thickness.

grain structure.¹³ For film thicknesses of W-Ti on silicon less than 150 nm, the STM micrographs of the surface showed that the deposit uniformly covers the substrate. With increasing thicknesses, agglomerates composed of several small grains were more expressed. The agglomerate appearance at the film surface coincides with the rapid increase of the grain size for thicknesses over 150 nm. The dimensions of agglomerates are about 100 nm. It is more likely that the formation of agglomerates is caused by nucleation and formation of thin films, than as a characteristic of the employed substrate.

The surface roughness also depends on the thin film thickness. The average surface roughness, measured using the STM cross-section program, increased with film thickness, as shown in Fig. 6. It is about 0.3–0.5 nm for small thicknesses, which is smaller or the same as the initial surface roughness of the silicon substrate.

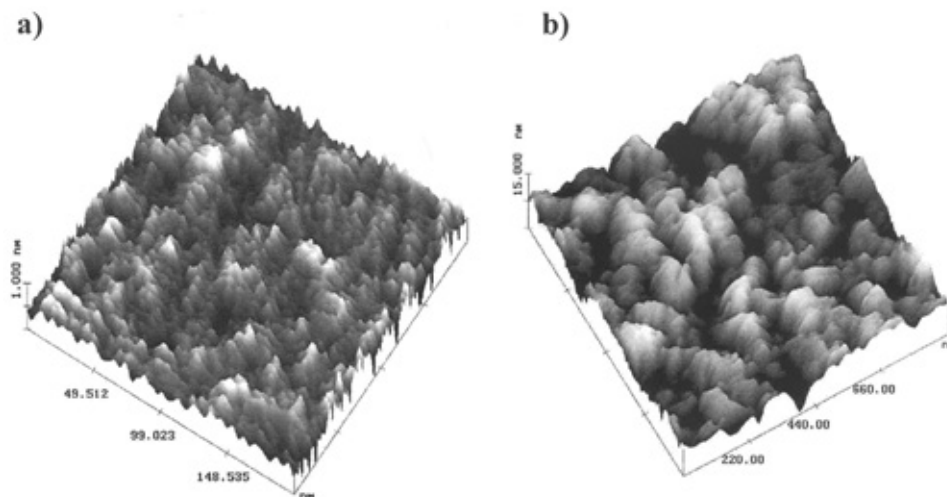


Fig. 5. STM Images of W-Ti thin films of thickness: a) 10 nm and b) 900 nm.

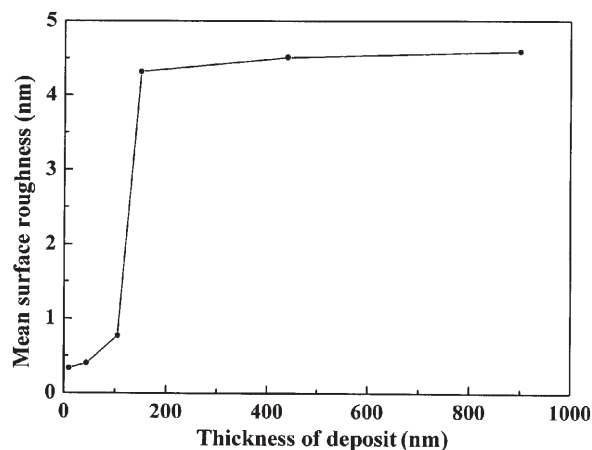


Fig. 6. Mean surface roughness of W-Ti thin films as a function of thickness.

Obviously, filling the gaps of the substrate surface occurs in the first step of thin film formation. The roughness rapidly increase up to 3.5 nm with further increasing of the film thickness. Finally, for film thicknesses of 150 nm and greater, the roughness slowly increases to about 4.5 nm for 900 nm thick films. The rapid change of the surface roughness coincides with the changes of the grain size. Just as in the case of the grain size *vs.* the thickness, the increase in surface roughness with increasing film thickness is due to the formation of agglomerates.

CONCLUSION

The results show that the structural and morphological characteristics of nanometer sputtered W-Ti thin films depend on the film thickness. These changes were investigated in the range from 10 nm to 900 nm. A small signal corresponding to the thin film together with one of the silicon substrate can be observed in the XRD spectrum for thicknesses below 150 nm. Simultaneously, thin films have polycrystalline form with a fine grain structure and small surface roughness (the filling the gaps process dominates). For the W-Ti thin films with thicknesses above 150 nm, a signal corresponding to the substrate is no longer observed, while an intensive signal of the deposit confirms a polycrystalline film structure composed of a b.c.c. W phase, (110) orientation, with the presence of a h.c.p. Ti phase, (101) orientation. In the same thickness range, the formation of agglomerates occurs yielding a progressive increase in the grain size, as well as of the mean surface roughness. The critical thickness at which the investigated structural and morphological characteristics change drastically is 150 nm.

The results obtained by the LEIS method showed that the surface composition of W-Ti thin films is significantly different from the expected composition of the interior of the thin films. The major reason is the presence of oxygen at the surface, which is the driving mechanism for the segregation of the titanium surface.

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ИЗВОД

СТРУКТУРА И МОРФОЛОГИЈА НАНОМЕТАРСКИХ W–Ti/Si ТАНКИХ СЛОЈЕВА

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Истраживања структурних и морфолошких карактеристика волфрам–титанских (W–Ti) танких слојева извршена су на депонованом материјалу нанометарских димензија. Танки слојеви су депоновани катодним распршивањем на силицијумској подлози. Рад обухвата проучавање утицаја дебљине депозита на структурне и морфолошке карактеристике W–Ti танких слојева на нанометарској скали. Фазни састав и величина зрна одређени су дифракцијом X-зрака (XRD), док је морфологија површине и средња површинска храпавост одређена сканирајућом тунелском микроскопијом (STM). Танки слојеви имају поликристалну структуру сачињену од запремински централне кубне фазе W уз присуство хексагоналне фазе Ti. Максимум у XRD спектру на позицији угла 2θ у интервалу $38 - 43^\circ$ потиче од преклапања W(110) и Ti(101) равни. Хемијски састав површине танких слојева одређен је методом расејања јона ниске енергије (LEIS). Резултати показују присуство површинске сегрегације титана као и присуство кисеоника на површини.

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