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Analysis of surface properties of Ti-Cu-Ox gradient thin films using AFM and XPS investigations

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The paper presents results of investigations on surface properties of transparent semiconducting thin films based on (Ti-Cu)oxide system prepared using multi-magnetron sputtering system. The thin films were prepared using two programmed profiles of pulse width modulation coefficient, so called V- and U-shape profiles. The applied powering profiles allowed fabrication of thin films with gradient distribution of Ti and Cu elements over the thickness of deposited layers. Optical investigations allowed determination of transparency of prepared films that reached up to 60 % in the visible part of optical radiation, which makes them attractive for the transparent electronics domain. Surface properties investigations showed that the surface of mixed (Ti-Cu)oxides was sensitive to adsorption, in particular to carbon dioxide and water vapor. Soft etching with argon ions resulted in surface cleaning from residuals, however, deoxidation of Cu-oxide components was also observed.

Keywords: *surface; gradient distribution; thin film oxide*

1. Introduction

In recent years, a significant increase in designing, manufacturing and characterization methods for functional coatings based on gradient materials has been observed [1–3]. Their specific properties can be achieved e.g. by changing the composition of coating layer or by introducing stresses into the layer during the fabrication process (as a function of coating thickness). Thanks to that, it is possible to manufacture devices with new or significantly improved functional parameters compared to those fabricated using classical approaches. The highly developed trend in research on modern coating materials also successfully incorporates optical coatings for the use in transparent electronics [4, 5]. The material used for fabrication of such coatings should exhibit good transparency in the visible spectrum range and simultaneously good electrical conductivity (or semiconducting properties). Among others, surface properties of such coatings are also very important from practical point of view in different surface-sensitive applications, like for example, semiconducting oxide gas sensors [6], self-cleaning coatings [7], etc. In the present paper, the results of the analysis of surface properties of transparent semiconducting oxide thin films based on the (Ti-Cu)Ox system with gradient elements concentration has been presented. For the analysis, two types of thin films with similar composition but with different concentration profiles have been selected. In our previous paper [8] it was shown that selected films have outstanding electrical properties in terms of occurrence of memristive behavior. In the present paper, further analysis of surface properties performed using atomic force microscopy, X-ray photoelectron spectroscopy and surface elemental analysis has been presented.

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2. Experimental

The gradient thin films were prepared using multi-magnetron sputtering system [9] by co-sputtering two titanium (99.95 %) and one copper (99.99 %) discs positioned in a confocal configuration [10]. The films were deposited on silica glass and TiAlV conductive substrate by simultaneous pulse-DC sputtering of all the three targets. However, in order to obtain the gradient concentration, the pulse duration in which the power was delivered to each particular target was changed during the time of thin film growing by so called pulse width modulation method. Specifically, the power supplied to the two Ti discs was constant and fixed at its maximum level (pulse width modulation coefficient pwm = 100 %), whereas the pwm parameter for Cu target was changed in the way presented in Fig. 1.

In regard to applied profiles of pwm coefficient, the pwm profile were named as V- and U-shape (Fig. 1). The time of deposition of both films was 240 minutes and the resulting thin film thickness was 515 nm and 610 nm, for the thin film prepared with V- and U-shape profile, respectively. The thin film thickness was determined using Tylor Hobson CCI Lite optical profiler.

The morphology of the deposited film surface and its elemental composition were investigated by means of scanning electron microscope (FEI-Inspect S50) equipped with an elemental energy dispersion X-ray spectroscopy (EDS) detector. Also, an atomic force microscope (AFM), model TT-AFM Workshop, was used to obtain surface topography images on areas of up to 15 μm × 15 μm. In addition to the three-dimensional qualitative assessment of the topography, the AFM was able to determine quantitative parameters of the roughness amplitude - an essential component of a surface texturing aspect. The roughness values were recorded on a profile (line scan), which allowed us to obtain values of arithmetic mean deviation (Ra), representing arithmetic average of recorded absolute values and values of root mean square deviation (RMS) that define the standard deviation of the profile height distribution.

Optical properties were recorded using Ocean Optics CCD spectrophotometers (QE6500 and NIR512-2.1) and a coupled deuterium-halogen lamp. The transmission and reflection spectra were collected over a visible and near-infrared range from ca. 200 nm to 2100 nm.

The results of structure (including results from X-ray diffraction (XRD) and transmission electron microscopy (TEM) investigations) and elemental profile investigations have already been provided in the literature [11]. The films were XRD-amorphous and the elemental investigations performed using TEM confirmed the gradient distribution of Cu component in the films possible to obtain using the pwm powering profiles (Fig. 1).

The XPS measurements of the prepared (Ti-Cu)Ox structures were performed using hemispherical electron analyzer with an X-ray source power supply unit SPECS HSA 3500 by AlKα line (1486.6 eV). The recorded spectra were calibrated using a standard procedure with respect to the C1s photoelectron peak.

3. Results

3.1. Optical properties

Transparent oxide semiconducting thin films are of great interest for rapidly developing domain of transparent electronics. Such films should be characterized simultaneously by good optical transparency in the visible part of optical radiation spectrum, and good electrical conductivity. Fig. 2 presents recorded spectra for both thin films prepared using different (V- and U-shape) pwm profiles.

The shape of recorded transmission T and reflection R spectra was quite similar and one can see that the prepared thin films were relatively well transparent in the visible part of optical radiation (Fig. 2). Visible maxima and minima result from multiple interferences of the light reflected from air-thin film and thin film-SiO_2 substrate. As can be deduced from Fig. 2, transmission through the film produced with U-shape pwm profile is significantly reduced as compared to the sample prepared

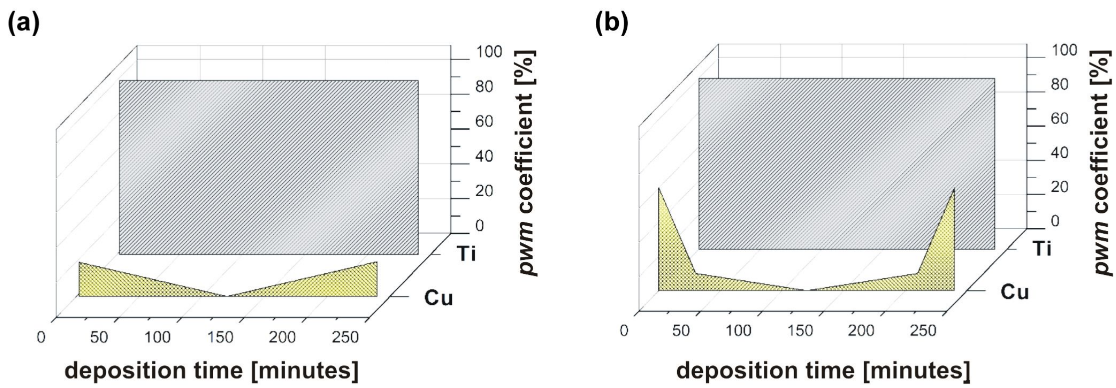

Fig. 1. Profiles of pwm coefficient of Ti and Cu targets powering during deposition of (Ti-Cu)Ox thin films, named with respect to the shape of the powering profile of the Cu target as: (a) V-shape, (b) U-shape.

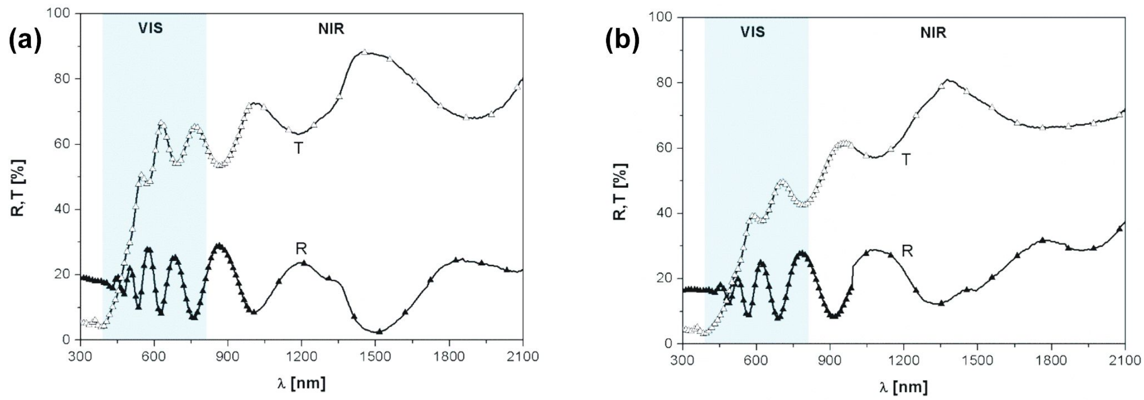

Fig. 2. Optical transmission and reflection spectra of (Ti-Cu)Ox thin films with different shape of magnetron powering profile: (a) V-shape, (b) U-shape.

with V-shape pwm profile of the Cu target powering. The average transmission in case of Fig. 2a is at the level of about 60 % whereas in Fig. 2b it does not exceed more than 50 % in the wavelength range from 500 nm to 1000 nm. A relatively sharp absorption of the light – λ_{cutoff} – occurs in the range of 410 nm to 470 nm for both investigated samples. In the infrared, the transparency of both thin films is higher and reaches even 70 % on average. Recorded optical spectra allowed us to determine the optical band-gap width for the allowed indirect transitions. Detailed parameters derived from the optical spectra are collected in Table 1.

Taking into account the composition of prepared films it may be concluded that reduced transmission of obtained films is a result of mixing of transparent insulating TiO_2 (band-gap width of 3.1 eV to 3.2 eV) with semiconducting CuO, Cu_2O (band-gap widths 1.2 eV to 1.5 eV; 2.1 eV to 2.6 eV). As a result, the films with intermediate properties were prepared. The optical properties are in agreement with electrical properties determined for the investigated films. The film prepared with the U-shape pwm profile had better conductivity (lower resistivity), yet it was less transparent. It is also worth noting, that both prepared films had p-type of electrical conduction which is extremely attractive for the purpose of fabrication of transparent devices in the field of transparent electronics.

3.2. Surface and elemental composition

3.2.1. SEM, EDS investigations

The average elemental compositions of investigated samples have been collected in Table 2.

Table 1. Selected optical and electrical properties of (Ti-Cu)Ox thin films prepared using different pwm powering profiles.

(Ti-Cu)Ox sample profile	thickness [nm]	ρ [$\Omega \cdot$cm]	E_g^{opt} [eV]	λ_{cutoff} [nm]
V-shape	515	2.86×10^6	1.88	470
U-shape	610	5.08×10^2	1.50	416

Table 2. Elemental composition of prepared (Ti-Cu)Ox thin films with different profile of elements gradient concentration.

(Ti-Cu)Ox pwm profile	TiO_2 [%]	CuO [%]
V-shape	52	48
U-shape	48	52

Overall amount of Cu in samples with V- and U-shape profiles were very similar and close to 50:50 mol% of TiO_2 and CuO oxides.

Fig. 3 presents images recorded using scanning electron microscope together with maps presenting elemental distribution of particular components, i.e. copper, oxygen and titanium.

The SEM surface images show relatively smooth, homogenous, crack-free surface with visible grains of 10 nm to 30 nm in lateral size. The distribution of each particular element in the EDS maps is also homogenous, e.g. no whiskers or clusters of particular material have been observed.

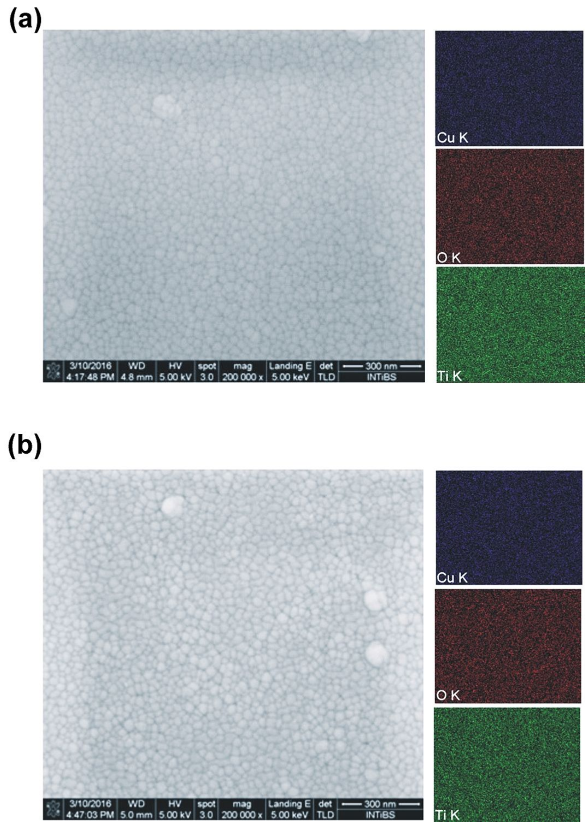

Fig. 3. SEM and EDS surface maps of Cu, O and Ti of prepared: (a) $Ti_{52}Cu_{48}Ox$ and (b) $Ti_{48}Cu_{52}Ox$ thin films.

3.2.2. AFM investigations

The results of AFM surface investigations are presented in Fig. 4 for $Ti_{52}Cu_{48}Ox$ (V-shape sample) and in Fig. 5 for $Ti_{48}Cu_{52}Ox$ (U-shape sample) prepared thin films.

The AFM analysis of the investigated samples confirmed the observations performed using SEM. The surface of prepared films was very smooth that was proven by relatively small values of root mean square RMS parameter. However, it was observed that the decrease in the overall Ti content and, at the same time, the increase in Cu concentration in the volume of the films resulted in a decrease of the surface roughness from RMS = 2.85 nm for the $(Ti_{52}Cu_{48})O_x$ to RMS = 1.75 nm for the $(Ti_{48}Cu_{52})O_x$ thin film. As one can see in Fig. 4 and Fig. 5, the $(Ti_{52}Cu_{48})O_x$ thin film is composed from smaller grains that is confirmed also by smaller dimension in Z direction (Sa = 7.76 nm and Sa = 5.57 nm and the histogram distributions in Fig. 4 and Fig. 5). Additionally, taking into account the profile of the pwm powering coefficient (Fig. 1), it is suspected that the surface of the thin film prepared using the U-shape profile would have higher content of Cu, that also may influence the observed surface roughness.

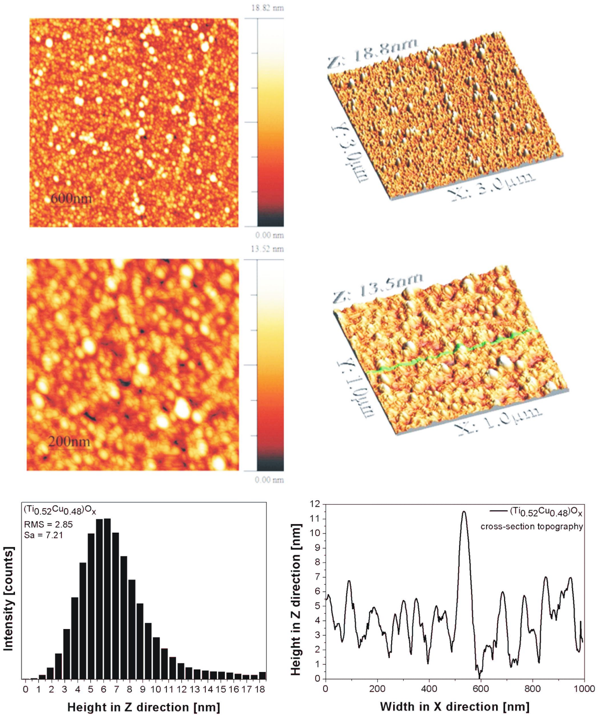

Fig. 4. AFM results of surface investigations of $Ti_{52}Cu_{48}Ox$ V-shape thin film.

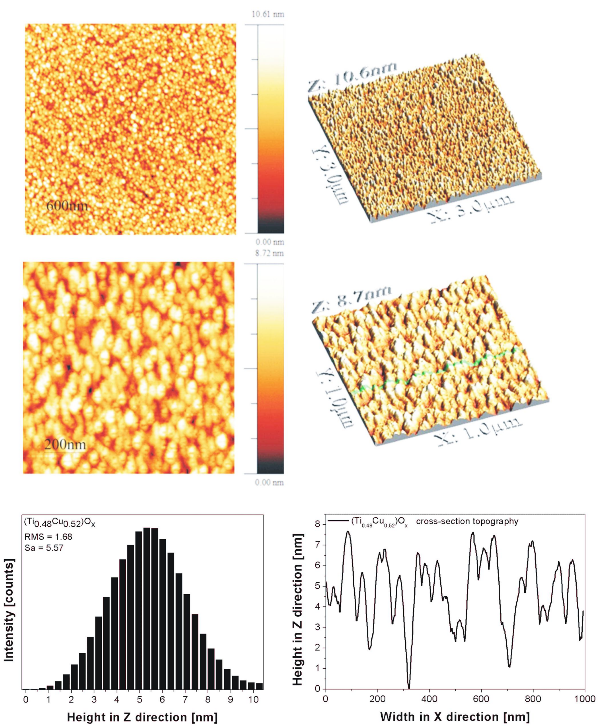

Fig. 5. AFM results of surface investigations of $Ti_{48}Cu_{52}Ox$ U-shape thin film.

3.2.3. XPS investigations

Fig. 6 and Fig. 7 present high resolution X-ray photoelectron spectra for C1s, O1s, Ti2p and Cu2p peaks recorded for prepared $(Ti_{52}Cu_{48})O_x$ and $(Ti_{48}Cu_{52})O_x$ thin films.

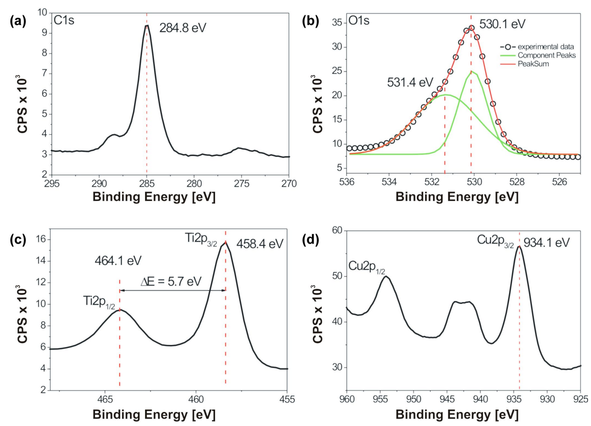

Fig. 6. High resolution XPS spectra of: (a) C1s, (b) O1s, (c) Ti2p and (d) Cu2p obtained for $(Ti_{52}Cu_{48})Ox$ thin film.

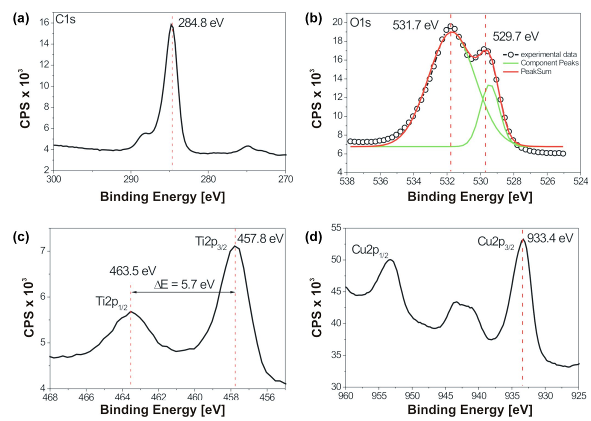

Fig. 7. High resolution XPS spectra of: (a) C1s, (b) O1s, (c) Ti2p and (d) Cu2p obtained from $(Ti_{48}Cu_{52})Ox$ thin film.

The XPS spectra show high intensity of recorded C1s photoelectron peak and a strong shoulder in the higher energy range in the run of recorded O1s spectra which indicates the presence of contaminations on the surfaces of both deposited films.

Such contaminations are related mostly to carbon dioxide and water vapor resulting from the fact that both samples were exposed in similar conditions to an air ambient before the XPS experiment.

The deconvolution of the O1s peaks showed clearly that they were composed from two peaks: O1s centered at 531.7 eV which may be connected with the adsorbed water or with the presence of hydroxyl groups on the surface [12, 13] and the O1s peak centered at about 530.1 eV (or 529.7 eV) that may be attributed to the Cu_2O and the TiO_2 [13, 14]. Taking into consideration the intensity of the C1s peaks shown in Fig. 6a and Fig. 7a and the component peaks centered at about 531.7 eV it might be concluded that the surface of $(Ti_{48}Cu_{52})Ox$ thin film (prepared using the U-shape pwm powering profile) is more likely to adsorb carbon and water from the surrounding environment than the $(Ti_{52}Cu_{48})Ox$ one. The positions of recorded peaks for Ti2p and Cu2p photoelectron peaks are typical of TiO_2 and CuO or (Cu_2O).

Analysis of surface species performed based on XPS spectra in connection with AFM investigations suggests that the higher content of copper in the U-shaped sample surface favors oxygen and carbon adsorption more than higher surface diversity that was observed in case of the thin film prepared using the V-shape powering profile.

In order to remove the residual surface species, prepared samples were cleaned with soft Ar ions bombardment. The cleaning process was conducted by supplying the ion gun with I = 3 mA current. The cleaning process lasted 20 min for each thin film. In Fig. 8 and Fig. 9 the XPS measurement results after ion sputtering of the samples have been presented.

The analysis of the XPS spectra of investigated samples after the ion-cleaning process showed significant removal of C1s contaminations from the samples surfaces (Fig. 8a and Fig. 9a). Furthermore, the high resolution XPS spectra for O1s (Fig. 8b and Fig. 9b) showed a decrease of the intensity of oxygen and lack of a signal from the oxygen connected with OH^- or water molecules. Taking into consideration the photoelectron spectra for Cu2p peaks of the investigated samples, it is worth

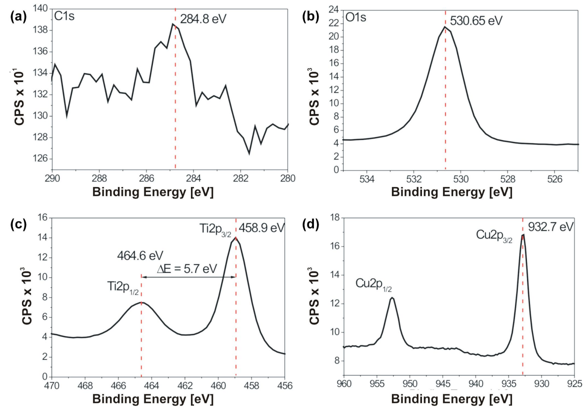

Fig. 8. High resolution XPS spectra of: (a) C1s, (b) O1s, (c) Ti2p and (d) Cu2p obtained from $(Ti_{52}Cu_{48})Ox$ sample after soft cleaning process.

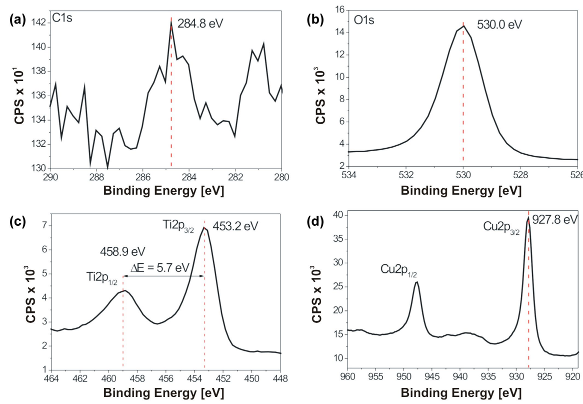

Fig. 9. High resolution XPS spectra of: (a) C1s, (b) O1s, (c) Ti2p and (d) Cu2p obtained from $(Ti_{48}Cu_{52})Ox$ sample after soft cleaning process.

to notice that ion bombardment changed the oxide phase of CuO into more Cu metallic phase.

Table 3 presents the calculated from the recorded XPS spectra relative atomic concentration ratios of particular components on the surfaces of investigated samples before and after ion-cleaning process. As results from the table, after cleaning process, carbon and oxygen concentration on the surface decreased for both investigated samples. As it comes to Ti, its relative atomic concentration increased of about two times for both samples after ion-cleaning. However, it can be observed that for Cu2p, the relative atomic concentration in case

Table 3. Calculated relative atomic concentration before and after soft cleaning process for the investigated (Ti-Cu)Ox thin films.

	$(Ti_{52}Cu_{48})O_x$ V-shape pwm profile		$(Ti_{48}Cu_{52})O_x$ U-shape pwm profile	
	before surface cleaning	after surface cleaning	before surface cleaning	after surface cleaning
Element	Relative atomic concentration [%]	Relative atomic concentration [%]	Relative atomic concentration [%]	Relative atomic concentration [%]
O1s	65.92	63.27	71.61	42.29
C1s	0.69	0.57	1.78	0.77
Cu2p	20.97	11.03	21.49	31.98
Ti2p	12.41	25.13	5.13	12.48

of $(Ti_{52}Cu_{48})$Ox (V-shape pwm profile) thin film decreased whereas for the $(Ti_{48}Cu_{52})O_x$ sample the Cu concentration increased. That could be interpreted as a more metallic behavior of the thin film surface. This conclusion is supported also by calculation of the position of valence band maximum with respect to Fermi level (Table 4). The negative value may indicate that the valance band and conduction band overlap each other in the investigated sample, which is typical of metallic materials. The obtained result is also in agreement with the programmed U-shape pwm powering profile. As results from Fig. 1, during last 20 minutes of deposition of the thin film, the power delivered to the magnetron equipped with the Cu target was up to 60 % of the maximum power, that is three times more than for the thin film prepared using the V-shape of the pwm powering profile.

Table 4. The valance band maximum (VBM) values obtained for (Ti-Cu)Ox samples.

(Ti-Cu)Ox sample profile	VBM [eV] before surface cleaning	VBM [eV] after surface cleaning
$(Ti_{52}Cu_{48})O_x$ V-shape	0.83	0.77
$(Ti_{48}Cu_{52})O_x$ U-shape	0.44	−0.34

4. Conclusions

In this paper, the results of optical and surface properties investigations of transparent semiconducting thin films based on the (Ti-Cu)Ox system have been presented. Even if the overall elemental composition in the prepared samples was very similar, the optical investigations showed that the transparency and the optical band gap width were slightly reduced for the thin film prepared using the U-shape of the pwm powering profile (Fig. 2). Simultaneously, the resistivity of this thin film was also reduced which resulted in its better conductivity.

Performed investigations using the AFM analysis allowed us to conclude that, the applied powering profile affected the roughness of the surface and the grains distributions. The RMS parameter for the $(Ti_{48}Cu_{52})O_x$ (U-shape pwm powering profile) was lower and the distribution of the height in Z direction was more symmetrical (Fig. 5).

Performed XPS investigations allowed us to conclude that the samples were very sensitive to exposure to ambient atmosphere which makes them interesting as a prospective structures for gas sensing devices. Analyses performed after soft ion cleaning support the conclusion about higher concentration of copper near the surface resulting from the applied profiles of pwm coefficient.

Acknowledgements

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