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Surface and Electrical Characterization of Non-Stoichiometric Semiconducting Thin-Film Coatings Based on Ti-Co Mixed Oxides Obtained by Gas Impulse Magnetron Sputtering

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Abstract: This article presents a detailed investigation of non-stoichiometric (Ti,Co)O_x thin films prepared using the Gas Impulse Magnetron Sputtering (GIMS) technique. The films were prepared with various Co contents (3 at.%, 19 at.%, 44 at.%, and 60 at.%) and characterized for their material composition, microstructure, and electrical properties. The films exhibited an ohmic behavior with linear current-voltage (I-V) characteristics, and their resistivity values ranged from approximately 10^{−3} to 10⁴ Ω·cm. The highest resistivity was observed in the film with 3 at.% Co content. Thermoelectric measurements revealed that all of the prepared films displayed n-type semiconducting properties, with the Seebeck coefficient (S) tending close to zero. The resistivity of the films decreased as the temperature increased, affirming their semiconducting nature. The activation energy (E_a) values, determined using the Arrhenius formula, ranged from 0.0058 eV to 0.267 eV, with the highest E_a observed for films containing 3 at.% Co. Additionally, the films' surface topography and microstructure were examined through Atomic Force Microscopy (AFM) and optical profiler techniques. The results showed that the films had smooth, crack-free surfaces with remarkable homogeneity. The surface diversification decreased with the increase in cobalt in the (Ti,Co)O_x films.

Keywords: non-stoichiometric oxide thin films; TiO_x; (Ti,Co)O_x; CoO_x; gas impulse magnetron sputtering; n-type semiconductor



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1. Introduction

The electrical properties of titanium oxides and cobalt oxides have been fairly well studied and described in numerous research papers [1–11]. As is well known, one of the most important electrical parameters determining the properties of such materials is their resistivity (ρ). In the case of titanium oxides, the most commonly described form is titanium dioxide. The resistivity value of TiO₂ depends both on the synthesis method and the form in which it is produced, such as thin films, nanoparticles, nanowires, etc. (Figure 1) [1–3,12–18]. In the case of titanium dioxide-based materials, the resistivity typically falls within the range of 10^{−3} to 10⁸ Ω·cm [19]. In Figure 1, a comparison of the resistivity of materials based on TiO₂ manufactured using the PVD (Physical Vapor Deposition) method and LPD (Liquid Phase Deposition) is presented. As can be observed, the resistivity of these materials differs by several orders of magnitude, highlighting the significant influence of the manufacturing technology on the electrical properties of such nanomaterials. Cobalt oxides (i.e., Co₃O₄) also exhibit similar resistance values, which are largely dependent on the method of their preparation. However, post-processing treatment also plays a significant role. Subjecting materials based on Co₃O₄ to high-temperature annealing results in a significant increase in resistivity values compared to materials that have not undergone such treatment (Figure 2) [6–11,20,21]. It is important to note that the majority of research focuses mainly on characterizing cobalt oxides in the form of Co₃O₄

rather than cobalt oxides in the form of CoO, which is attributed to significant challenges in obtaining the latter form [22]. However, it should be noted that in the case of oxide materials containing both of these elements, only single publications are available that discuss the issue of their resistivity [23,24].

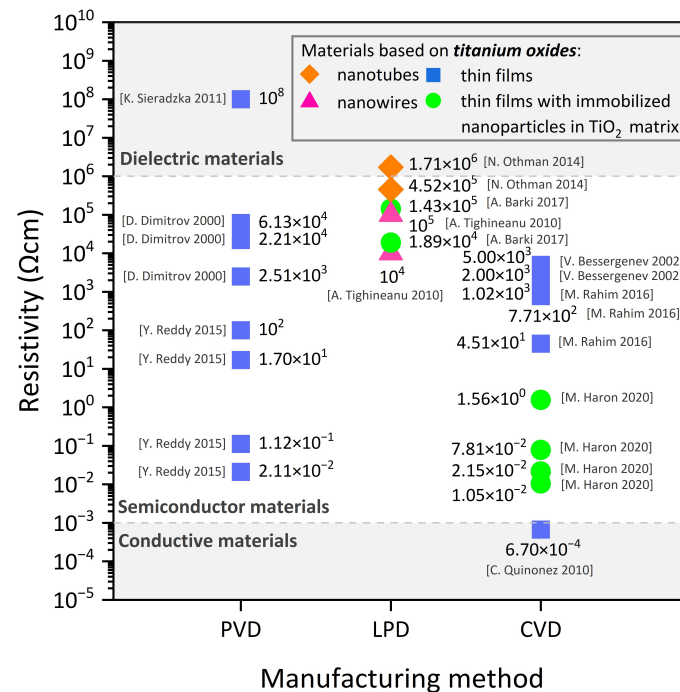


Figure 1. The resistivity of titanium-based oxides depends on their manufacturing method and form [1–3,12–18]. Abbreviations: PVD-Physical Vapor Deposition; LPD-Liquid Phase Deposition.

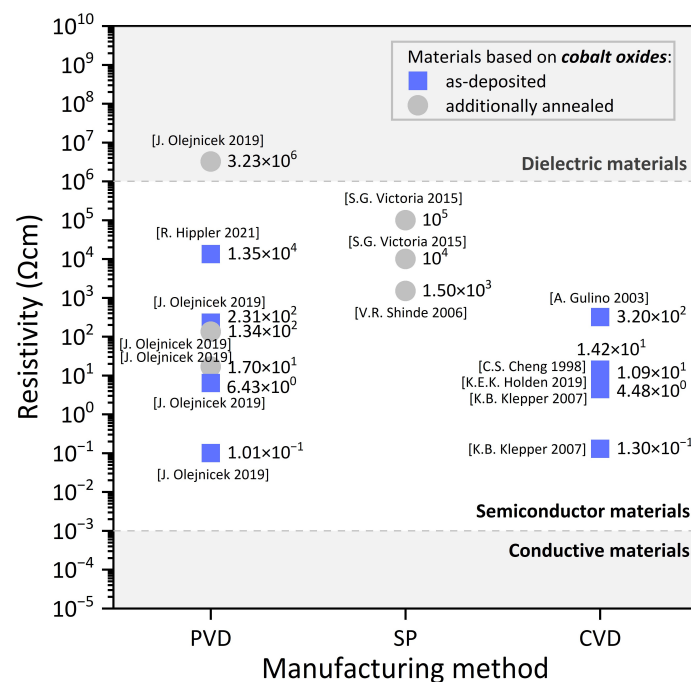


Figure 2. The resistivity of cobalt-based oxides depends on their manufacturing method and additional annealing [6–11,20,21]. Abbreviations: PVD-Physical Vapor Deposition; SP-Spray Pyrolysis; CVD-Chemical Vapor Deposition.

Another key parameter in electronics is the type of electrical conductivity. In the case of TiO_2 , strong electron conductivity (n-type) is observed [25–27]. TiO_2 displays n-type semiconducting properties due to a tendency for oxygen deficiency which manifests itself in the formation of either oxygen vacancies or titanium interstitials. Both of these phenomena are electron-type defects [28]. However, it is important to add that at high temperatures ($>900^\circ\text{C}$) and in strongly oxidizing atmospheres, titanium vacancies (V_{Ti}) are formed, causing TiO_2 to exhibit weak hole conductivity (p-type) [25,29–31]. Materials based on Co_3O_4 , on the other hand, exhibit a significantly different electrical conductivity character as they are p-type semiconductors [32–34]. No research indicating n-type conductivity has been found for materials based on cobalt oxide (II,III).

Of course, it should be emphasized that the type of conductivity in oxide materials can be modified through, for example, doping [32–44]. In the case of TiO_x , the most commonly used dopant to achieve hole-type conductivity is chromium [35–38]. Elements such as Mn [39], Al [40], and N [41] added to this matrix also allow the production of p-type materials. In contrast, multicomponent materials such as $\text{TiO}_x(\text{Nb, Mo, W})$ exhibit electron conductivity and are most frequently used for the detection of harmful gases to humans [38,42–44]. In the case of cobalt oxide, after introducing various dopants such as Ca [34], Cu [32], or Zn [33], p-type conductivity was achieved, and no changes in its type were observed. It is worth adding that there is a single publication regarding the use of cobalt as a dopant, but these ZnO:Co materials exhibit p-type conductivity [45].

One of the issues overlooked in the literature is the oxygen content in the manufactured nanomaterials, and as we know, the greater its amount, the greater the resistivity. In many processes, such as the sol-gel and chemical vapor deposition (CVD), the amount of oxygen added to materials is maximized, which is associated with the significant challenge of deposition, where one must precisely control the so-called oxygen deficit. Techniques like Gas Impulse Magnetron Sputtering (GIMS) allow for the controlled introduction of oxygen during the process, thereby enabling the fabrication of non-stoichiometric materials [46,47]. The initiation of pulsed discharge in the interelectrode zone of the magnetron and the generation of vapor/plasma for coating synthesis are consequences of pulsatile gas dosing. In the interludes between consecutive gas injections, the pumping system evacuates the injected gas and any residual material/target vapors, maintaining a pressure that prevents further discharges. The introduction of each new pulse of gas reinitiates the plasma process. The process chamber allows for the introduction of technological gases like argon and oxygen, their presence and quantity (flow rate) being dictated by the demands of the sputtering process, encompassing both reactive and non-reactive procedures. Non-stoichiometric thin films based on metal oxides, including titanium oxide and cobalt oxide, are also relatively less explored and represent an innovative research material. Currently manufactured titanium and cobalt oxides are well oxidized (at Ti^{4+} and Co^{3+} state) which results in receiving TiO_2 or Co_3O_4 forms. The transmission coefficient (T_λ) of TiO_2 in a form of anatase or rutile is generally around 80%. Unfortunately, such high transparency occurs with high resistivity [48]. The dielectric nature of such materials poses a problem, limiting the potential applications of these materials, such as their use in gas sensing devices, transparent oxide semiconductors, and more.

The current state of knowledge regarding the electrical properties of materials based on mixed titanium and cobalt oxides, as well as non-stoichiometric coatings, is notably deficient and replete with inconsistencies. A review of the current state of knowledge reveals a lack of comprehensive research on titanium and cobalt oxide materials (especially in non-stoichiometric form), which restricts the full utilization of the potential their combination can offer. Currently, only two reports exist on the electrical properties of oxide materials concerning mixtures of these two elements $(\text{Ti,Co})\text{O}_x$ [23,24], while research on materials based solely on titanium or cobalt oxides predominates (Figure 3). Therefore, the objective of this study was to fabricate films based on Ti and Co with varying material compositions, while reducing the oxygen content and achieving lower resistivity.

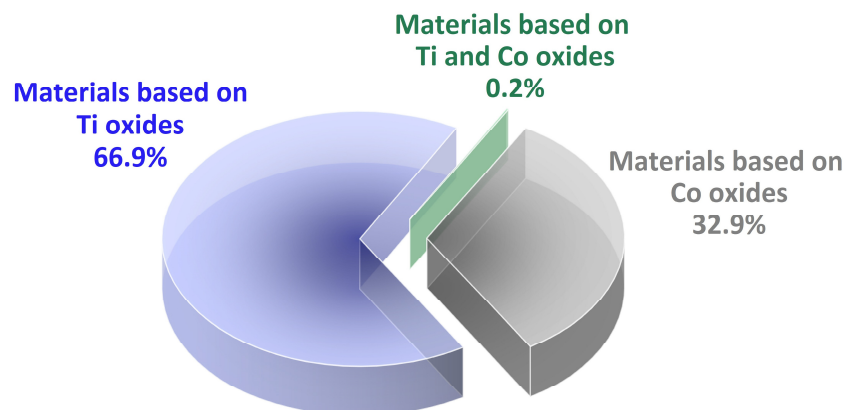


Figure 3. Publications related to electrical properties of oxide materials-based Ti and Co (based on the ScienceDirect database from 1980 to 2023).

2. Materials and Methods

2.1. Preparation of Thin Films

Nonstoichiometric $(\text{Ti,Co})\text{O}_x$ thin films with the desired material composition were prepared using the gas impulse magnetron sputtering method, referred to as GIMS. The magnetrons were supplied by an MSS2 2 kW pulsed AC power supply unit (DORA Power System, Wilczyce, Poland) [49–54]. The sputtering system was also equipped with vacuum gauges (Pfeiffer Vacuum, Asslar, Germany) and a gas flow control system that involves mass flow controllers (MKS Instruments, Andover, MA, USA). In the GIMS processes, a gas mixture of Ar and O_2 with a low O_2 content (in a ratio of 10:1) was injected directly into the working chamber onto the surfaces of metallic Ti, Co, and Ti-Co targets. These targets had a diameter of 30 mm, a thickness of 3 mm, and a purity of 99.95% and were mounted on the magnetron. Targets with Ti-Co compositions of 2 at.%, 12 at.%, and 50 at.% Co were used in the preparation. Targets were prepared using spark plasma sintering (SPS) with a system provided by FCT GmbH (Rauenstein, Germany) [55–57]. For sintering, Co and Ti nanopowders (99.95%, Kurt Lesker, Dresden, Germany) from the Lukasiewicz Research Network-Institute of Non-Ferrous Metals [46,57] were employed. A detailed description of the Ti-Co target preparation method can be found in a separate publication [48]. Multimagnetron configuration allowed for the deposition of $(\text{Ti,Co})\text{O}_x$ films with varying Co content (3 at.%, 19 at.%, 44 at.%, and 60 at.%). Furthermore, reference films of TiO_x and CoO_x were manufactured. A gaseous mixture comprising argon (Ar) and oxygen (O_2) was synthesized by means of a gas blending apparatus featuring a pair of distinct MKS mass flow controllers. The flow rates of argon (Ar) and oxygen (O_2) were configured at 30 sccm and 3 sccm, respectively. Gas impulses, introduced directly into the target, were synchronized with the MSS2 magnetron power supply unit, with each pulse cycle having a duration of 100 ms. The locally ignited plasma was generated at a pressure of less than 6×10^{-3} mbar, using a power supply delivering 500 W (500 V, 1 A). The ignition time for the plasma was 30 ms, and there was a 70 ms interval between successive pulses. The sputtering system was outfitted with both diffusion and rotary pumps. In the Gas Impulse Magnetron Sputtering (GIMS) procedures, the vacuum chamber was evacuated to a base pressure of approximately 5×10^{-6} mbar. Thin films were deposited onto silicon (Si) and silicon dioxide (SiO_2) substrates, with a separation distance of 16 cm between the target and the substrate.

2.2. Methods of Thin Films Characterization

An Atomic Force Microscope (AFM), specifically Nanosurf FlexAFM model from Liestal, Switzerland, was employed to assess the topographical alterations in the prepared thin films. The investigation employed contact mode imaging, utilizing force-modulated probes (with a spring constant of $k = 0.2$ N/m, WITec, Ulm, Germany). All experiments were conducted under uniform measurement conditions. The WSxM 5.0 Develop 10.2 software package [58] was utilized for the post-processing and analysis of the obtained data.

For all prepared films, the average size of grains was determined with the use of WSxM software and envelope method. These values were estimated based on 20 randomly selected grains at AFM image. The surface roughness of the prepared films was examined through non-contact measurement using a Taylor Hobson Tally Surf CCI Lite optical profiler (Talysurf CCI Lite, Leicester, UK). This equipment also facilitates the assessment of surface geometric properties, including surface flatness and thickness. The deposition rate was calculated based on the deposition time and the thickness of the resultant films. Electrical characterization was conducted using an M100 Cascade Microtech probe station (Cascade Microtech, Beaverton, OR, USA) in conjunction with a Keithley SCS4200 system. The current-voltage characteristics were obtained within a Faraday shield. These measurements, in combination with Arrhenius plots, played a pivotal role in the assessment of the resistivity of the as-deposited thin films. A comprehensive range of temperature-dependent resistivity measurements was performed across the spectrum of 300 K to 350 K, thereby facilitating the computation of the activation energy. For electrical characterization, an M100 Cascade Microtech probe station (Cascade Microtech, Beaverton, OR, USA) in conjunction with a Keithley SCS4200 system was also employed. Thermoelectric characteristics were obtained using the FLUKE 8846A voltmeter (Fluke, Everett, WA, USA) in conjunction with the Instek mK1000 temperature controller (GW Instek, Taipei, Taiwan). To determine the Seebeck coefficient, a controlled temperature gradient (ΔT) was established between the 'hot' and 'cold' electrical contacts, ranging from 0 to 50 K, with the 'cold' contact being maintained at room temperature.

3. Results and Discussion

3.1. Deposition Rate and Surface Topography of (Ti,Co)O_x Thin Films

The deposition rates of TiO_x, (Ti,Co)O_x, and CoO_x films were calculated, taking into account their thickness and sputtering time. The relationship between the Co content in (Ti,Co)O_x films and the sputtering rate during the sputtering process is illustrated in Figure 4. The quantity of cobalt in the target influences the deposition rates of the films. It can be observed that as the amount of Co increases, the deposition efficiency of the coatings nearly doubles. In the case of a film containing 3 at.% of Co, the deposition rate is nearly on par with that of TiO_x alone. This indicates that targets with Co sputter more efficiently because particles in the magnetic field have a greater tendency to adhere to the substrate. However, the sputtering rate of a film containing only cobalt oxide was lower due to its magnetic properties.

The surface topography was also assessed using an optical profiler for the prepared samples, covering an area of approximately 800 μm $\times$ 800 μm (Figure 5). The investigation results revealed that all films exhibited a crack-free, highly homogeneous, and smooth surface. The root mean square surface height (S_q) values of the TiO_x, (Ti_{0.97}Co_{0.03})O_x, (Ti_{0.81}Co_{0.19})O_x, (Ti_{0.56}Co_{0.44})O_x, (Ti_{0.40}Co_{0.60})O_x, and CoO_x thin films were measured at 1.92, 2.02, 1.86, 1.58, 1.39, and 1.19 nm, respectively (Figure 4). Tests carried out using optical profiler revealed a decrease in the S_q parameter with an increasing amount of cobalt.

The surface morphology of the TiO_x, (Ti,Co)O_x, and CoO_x thin films was examined using the AFM method, and the images of the deposited coatings are presented in Figures 6 and 7. In all cases, the film surfaces were free of cracks, exhibited remarkable homogeneity, and consisted of small grains. The grain size increased with the higher cobalt content from 35 nm to 61 nm, except for the film containing 44 at.% of Co, which exhibited a larger grain size of 102 nm. These AFM measurements corroborate the results obtained by scanning electron microscopy, as previously reported in our publication [46]. It is evident that with an increase in the Co content, the maximum height of the surface profile decreased significantly, ranging from 22.94 to 5.05 nm. Regarding the average surface height of the deposited coatings, the results revealed a Gaussian-like symmetrical distribution across all samples, indicating the excellent surface homogeneity (Figure 8). The root mean square surface roughness (RMS) values gradually decreased (four times) with increasing Co content in the (Ti,Co)O_x films. In the cases of the TiO_x, (Ti_{0.97}Co_{0.03})O_x, and (Ti_{0.81}Co_{0.19})O_x films,

the RMS value decreased only slightly from 2.09 to 1.87 nm. However, a further increase in cobalt content led to a significant alteration of the microstructure, resulting in a substantial reduction in the RMS value, falling within the range of 0.71 to 0.55 nm. Furthermore, the peak widths decrease fourfold with higher cobalt content, corroborating a common trend with the root mean square (RMS) roughness distribution (Figure 8). A similar trend was observed for the S_q parameter, with its value also decreasing as the amount of added cobalt increased.

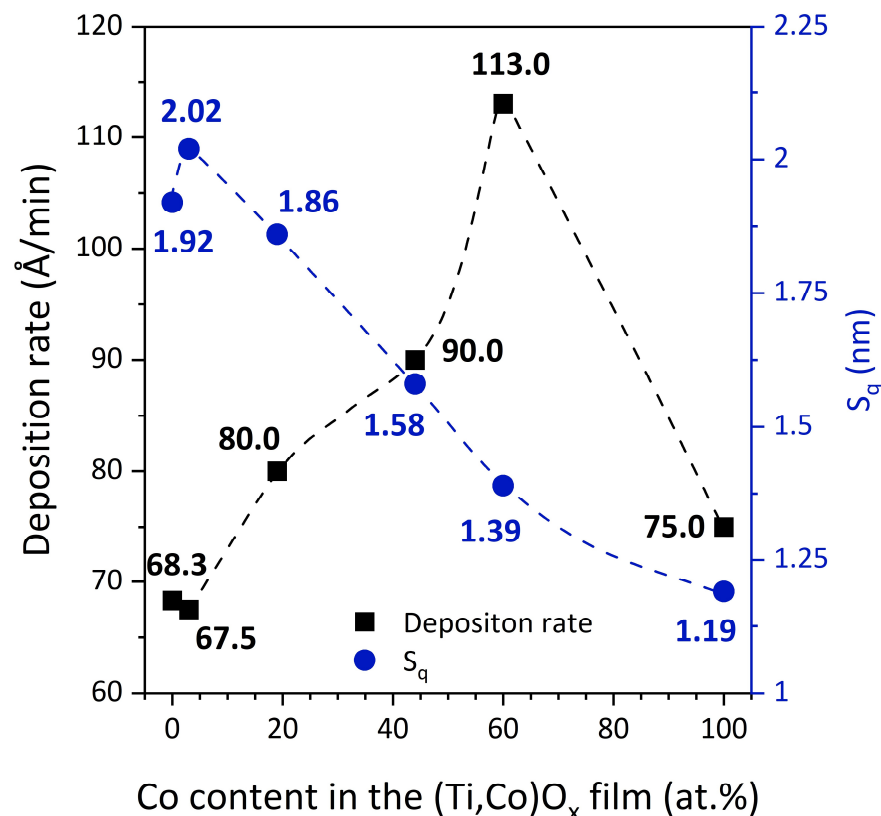


Figure 4. The influence of the Co content in the $(\text{Ti},\text{Co})\text{O}_x$ thin films on the deposition rate and their roughness. Designations: S_q -root mean square surface height value.

3.2. Electrical Properties of Thin Films

To evaluate the impact of Co content on the electrical properties of the TiO_x , $(\text{Ti},\text{Co})\text{O}_x$, and CoO_x thin films, current-voltage (I-V) characteristics and Seebeck coefficient measurements were conducted. The I-V characteristics of the prepared thin films were acquired in a planar configuration, and the results are depicted in Figure 9.

Each I-V characteristic displayed a linear relationship between voltage and current, indicating ohmic behavior across all the measured thin films. The resistivity values fell within the range of approximately 10^{-3} to $10^4 \Omega\cdot\text{cm}$, indicating substantial differences in electrical properties (Figure 10). The highest resistivity values were recorded for the thin film with 3 at.% of Co content, which also exhibited the steepest I-V characteristic among all the prepared films. However, it was observed that as the cobalt content increased in the films, the resistivity values successively decreased. These results are consistent with the optical properties, as very similar transmission spectra were obtained for these thin films, as previously presented in our publication [46]. Moreover, numerous studies also depict linear I-V behavior for titanium dioxide [5,59–62], and only isolated works showing non-linear changes in these characteristics can be found [62]. This indicates that the manufacturing method also determines the electrical properties of TiO_2 based materials. In the case of Co_3O_4 based materials, the I-V characteristics also exhibit a linear trend [63], but such studies are relatively infrequently presented in the literature [63].

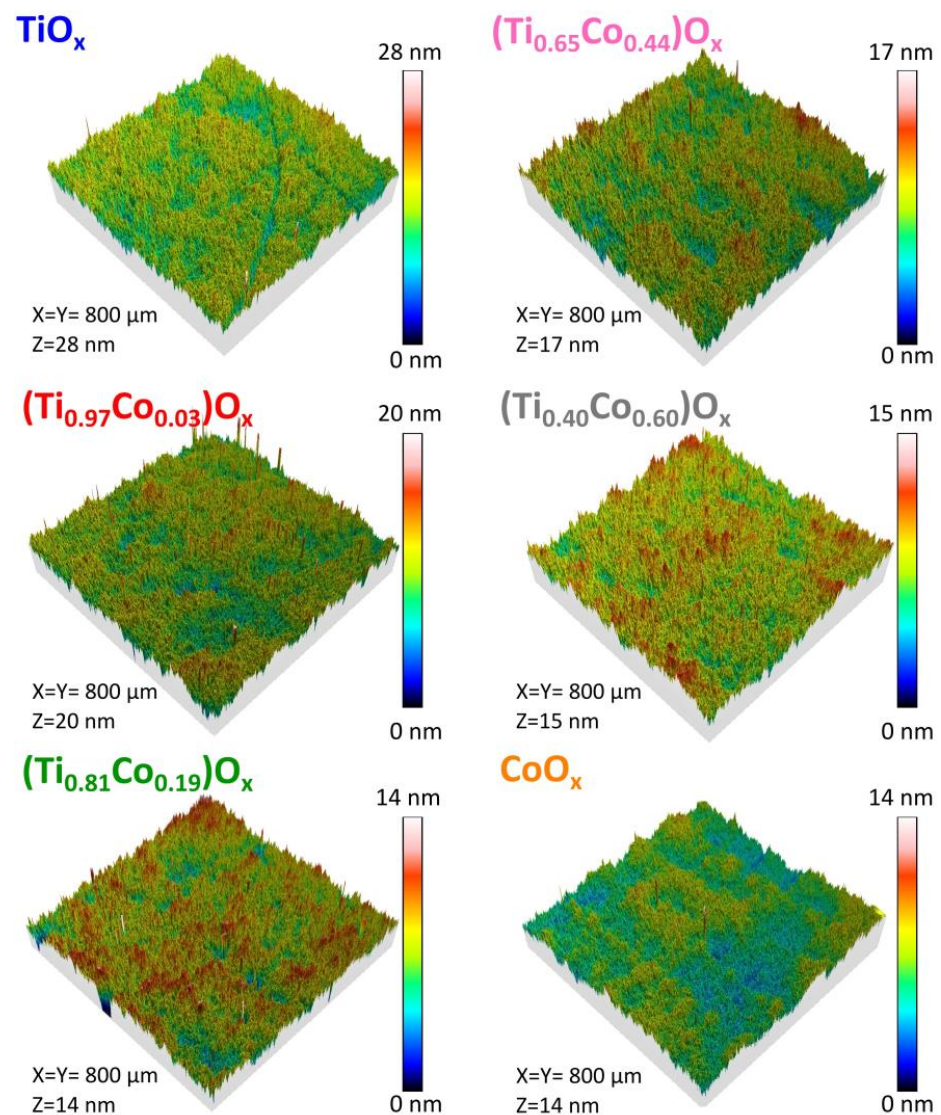


Figure 5. Three-dimensional surface profiles of TiO_x , $(\text{Ti,Co})\text{O}_x$, and CoO_x thin films.

Combining titanium oxides with cobalt oxides, i.e., manufacturing them in the form of mixtures, can result in obtaining a material with properties and advantages that are a combination of both. Depending on the manufacturing method, composition, and form, the mixtures of these oxides exhibit various tendencies, and currently, the influence of cobalt on their resistivity cannot be unequivocally determined [23,24]. It should be noted that while individual reports on the resistivity of films based on mixtures of titanium and cobalt oxides can be found, they typically concern materials with a high oxygen content. There is a lack of information regarding non-stoichiometric oxides. One noteworthy study for discussing the electrical properties of $(\text{Ti,Co})\text{O}_x$ is the work of M.Z. Musa and others [19]. It demonstrates that for thin films based on nanoparticles, the resistance decreases with an increase in the amount of cobalt, as indicated by the increasing slope in the I-V characteristic (Figure 10). In the study by Shreesha Bhat [24], it was shown that thin films based on TiO_2 with the addition of up to 2 at.% of Co exhibit an opposite tendency. With an increasing amount of cobalt, the I-V curve has a decreasing slope. Therefore, the nature of resistivity changes is also different, and it increases with the amount of Co in the film (Figure 10). These differences likely stem from the different manufacturing methods employed for these nanomaterials but also from their form.

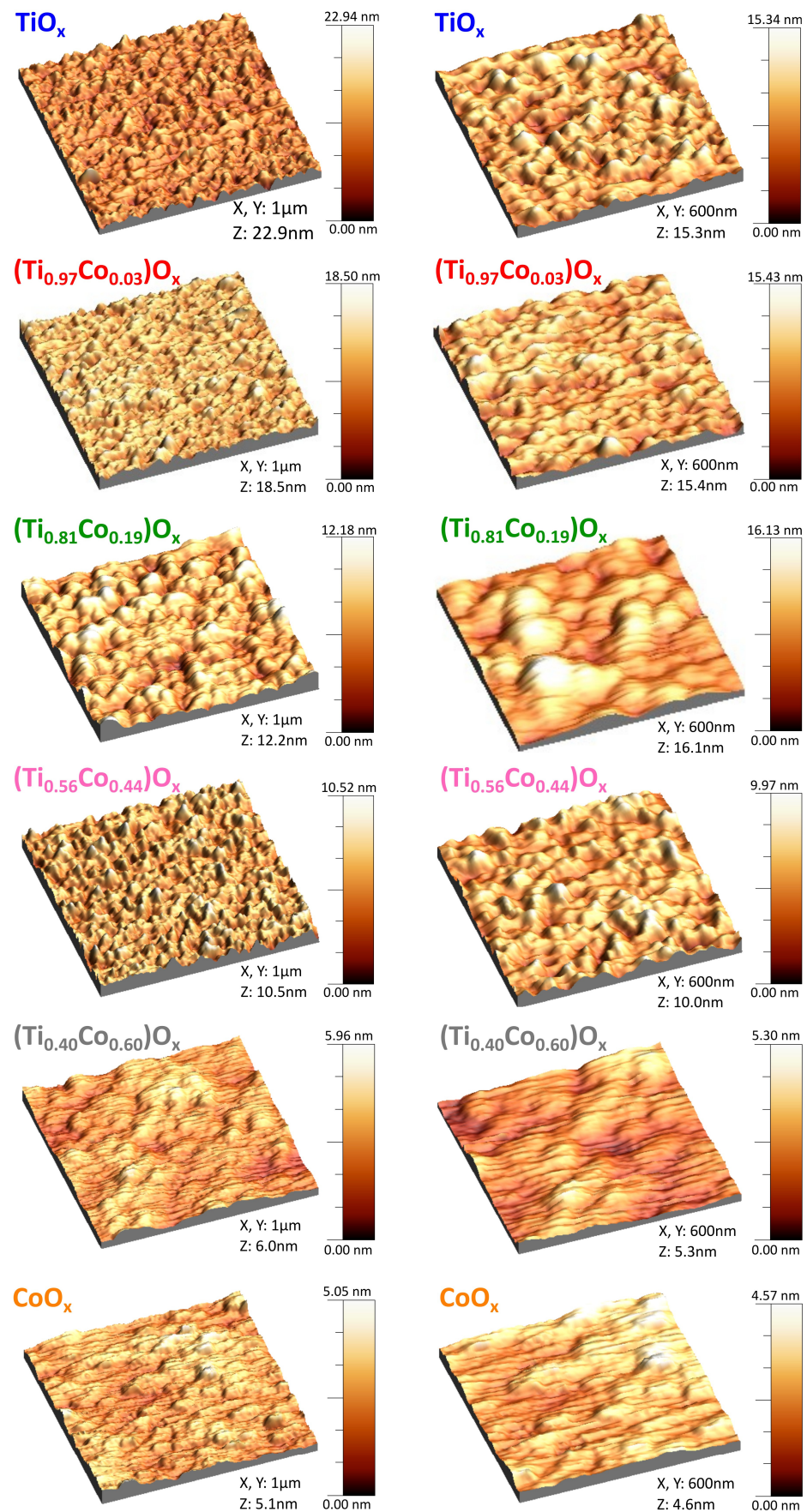


Figure 6. 3D AFM images of the surface of TiO_x , CoO_x , and $(\text{Ti,Co})\text{O}_x$ thin films.

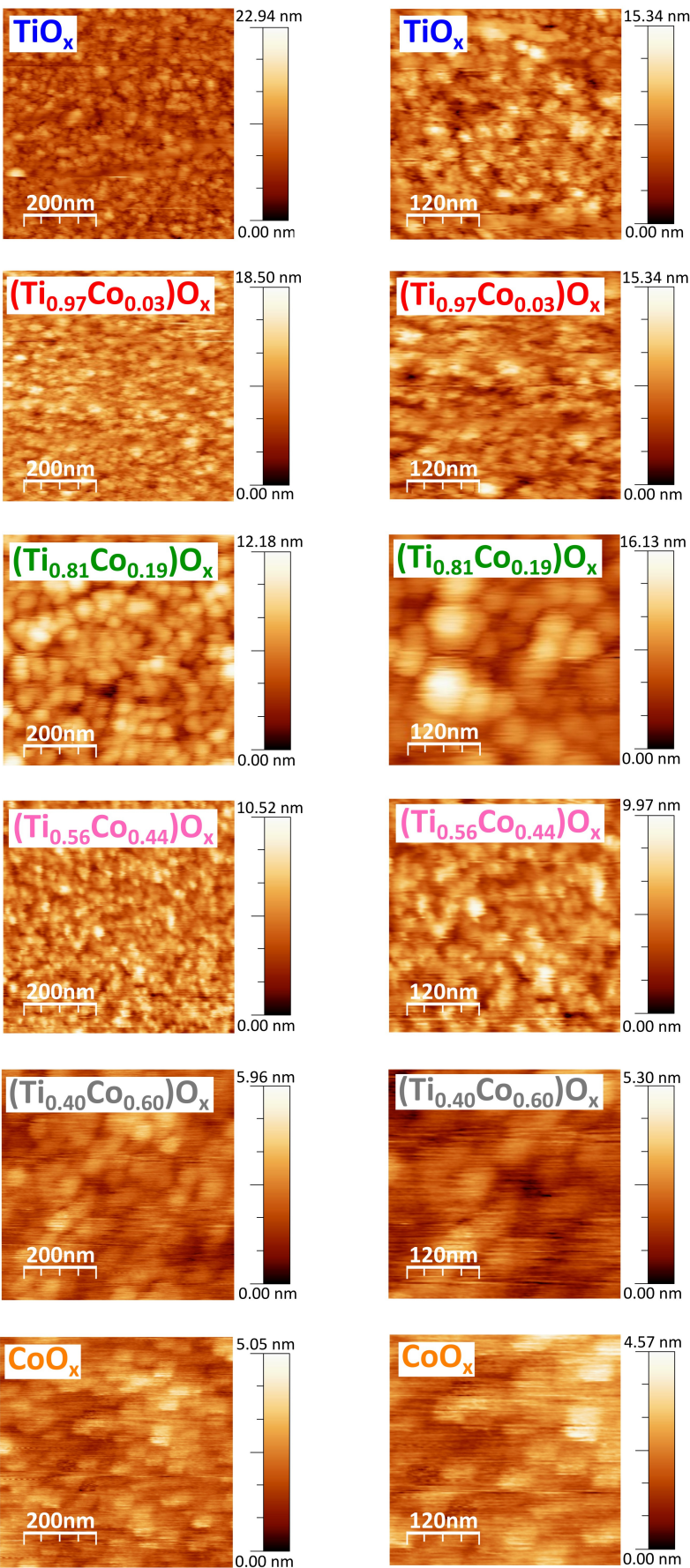


Figure 7. 2D AFM images of the surface of TiO_x , CoO_x , and $(\text{Ti},\text{Co})\text{O}_x$ thin films.

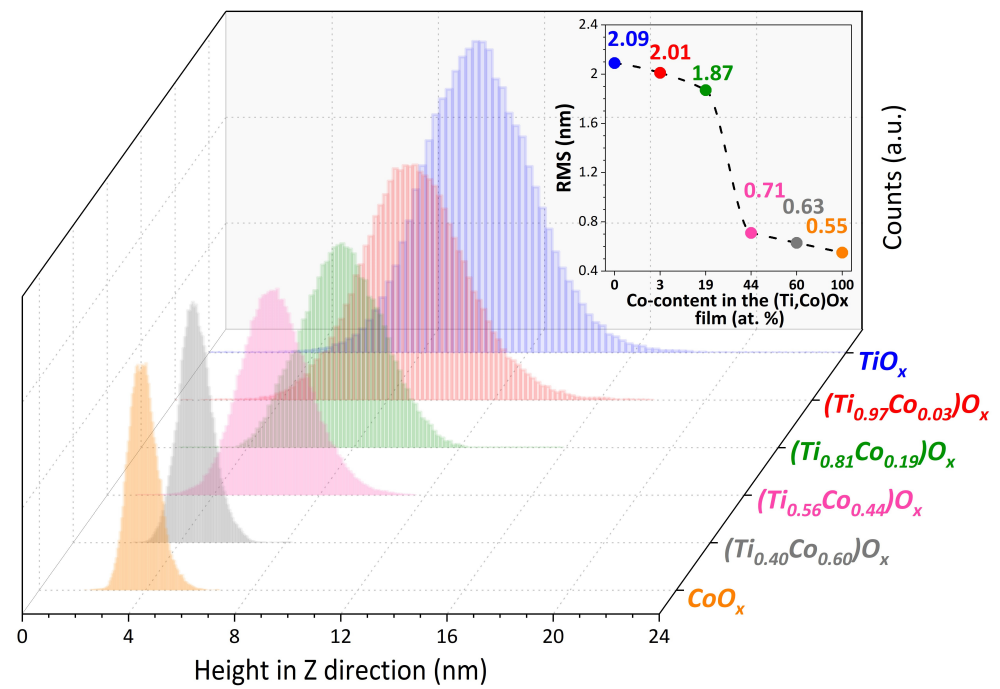


Figure 8. Surface height distribution of TiO_x , CoO_x , and $(\text{Ti,Co})\text{O}_x$ thin films.

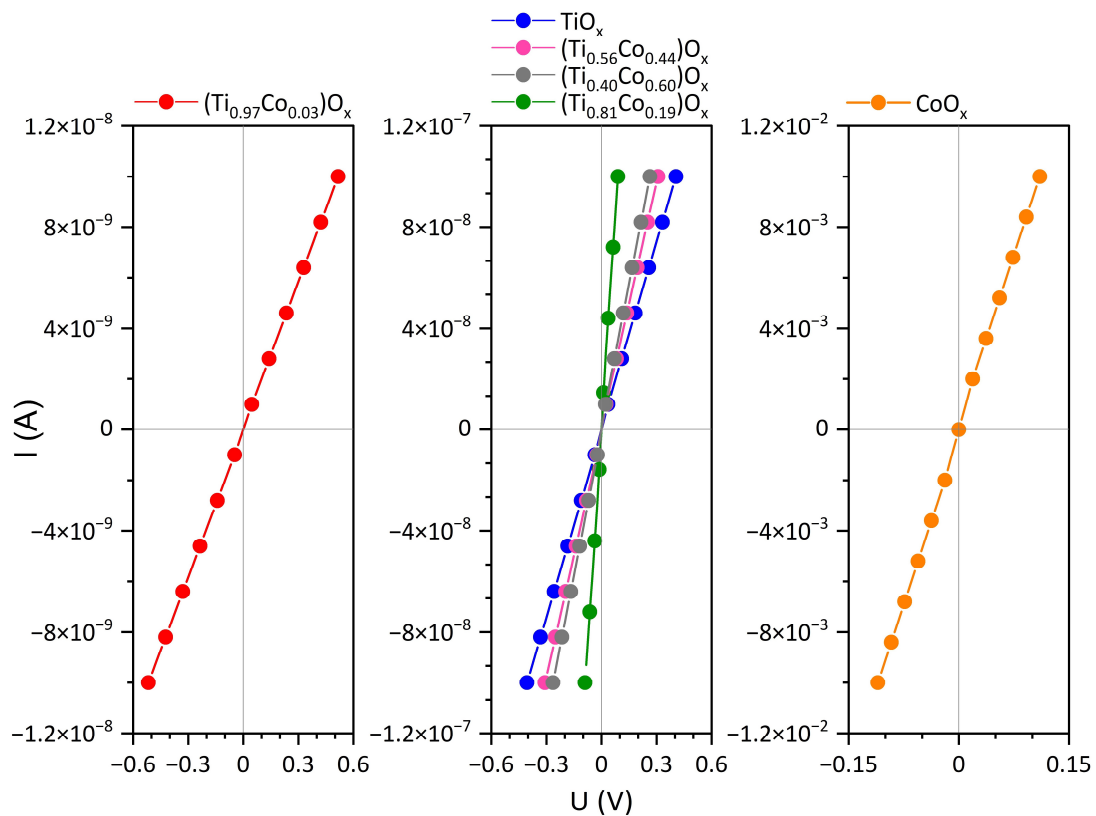


Figure 9. Current-voltage (I-V) characteristics (10 measurement cycles) of the prepared $(\text{Ti,Co})\text{O}_x$ films with varying cobalt concentrations.

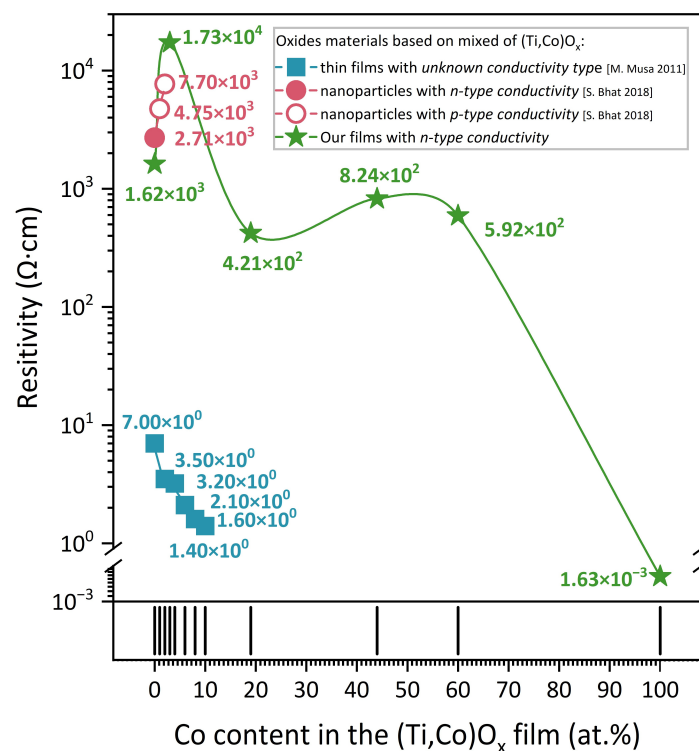


Figure 10. The effect of Co content on the resistivity (ρ) of our non-stoichiometric $(\text{Ti,Co})\text{O}_x$ thin films and exemplary films with immobilized nanoparticles in the TiO_x matrix and $(\text{Ti,Co})\text{O}_x$ nanoparticles, along with their current-voltage characteristics [23,24].

The electrical conduction characteristics of the TiO_x , $(\text{Ti,Co})\text{O}_x$, and CoO_x thin films were determined through thermoelectric measurements. In Figure 11a, the linear thermoelectric voltage (U_{Seebeck}) characteristics are shown as a function of the temperature difference ΔT between two opposing contacts on the prepared thin films. From the linear fitting of these thermoelectric characteristics, the Seebeck coefficient (S) was determined, as presented in Figure 11b. The negative S sign for all the prepared coatings indicates their n-type semiconducting properties. However, it is noteworthy that the values of this parameter (S) for all the films were close to zero, suggesting very weak n-type conductivity. The only existing literature [24] suggests that titanium and cobalt oxide-based nanomaterials may exhibit a type of conductivity labeled as 'p.' However, it is important to note that this parameter is derived from calculations rather than reliable scientific measurements (Figure 10). Moreover, our films were non-stoichiometric and a lack of oxygen could also be directly responsible for receiving of p-type (weak), which was also noted for CoO_x .

The conductivity of materials strongly depends on temperature, as the number of charge carriers (and, consequently, electrical conductance) increases exponentially with its rise. For this reason, based on the $\ln \sigma$ (T^{-1}) relationship, the activation energy (E_a) can be determined, which defines the energy required for an electron to transition from the valence band to the conduction band (for intrinsic semiconductors). As observed, their activation energy E_a assumes different values, ranging from 0.063 eV to 0.85 eV (Figure 12) [4,64–67]. For high activation energy values, the reaction rate is significantly temperature-dependent (intrinsic semiconductor). The smaller the activation energy (E_a), the less dependent the rate is on temperature (doped semiconductor). In the case of $E_a = 0$ eV, the reaction rate is independent of temperature (metals). In the case of TiO_2 , the type of crystalline structure has a significant influence on the value of E_a , among other factors. On the other hand, the activation energy for films prepared based on cobalt oxides ranges from 0.1 to even 1.6 eV. However, it can be observed that higher values of E_a (i.e., 0.21 to 1.6 eV) were determined for coatings that underwent additional heat treatment, which in the case of nanomaterials always leads to structural changes [6,9–11,63]. There is only one scientific report available

Figure 2 consists of two plots. Plot (a) shows the open-circuit voltage U (μV) versus the temperature difference ΔT (K) for various $(\text{Ti},\text{Co})\text{O}_x$ films. The y-axis ranges from -1.2×10^4 to 2×10^3 μV , and the x-axis ranges from 0 to 50 K. The legend indicates: TiO_x (blue circles), $(\text{Ti}_{0.97}\text{Co}_{0.03})\text{O}_x$ (red circles), $(\text{Ti}_{0.81}\text{Co}_{0.19})\text{O}_x$ (green circles), $(\text{Ti}_{0.56}\text{Co}_{0.44})\text{O}_x$ (pink circles), $(\text{Ti}_{0.40}\text{Co}_{0.60})\text{O}_x$ (grey circles), and CoO_x (orange circles). Plot (b) shows the Seebeck coefficient S ($\mu\text{V/K}$) versus the Co content in the $(\text{Ti},\text{Co})\text{O}_x$ film (at.%) from 0 to 100. The y-axis ranges from -2.5×10^2 to -5×10^1 $\mu\text{V/K}$. The legend is the same as in (a). The plot shows a dashed line representing the trend, with specific data points labeled: -224.4 (blue), -71.3 (red), -25.0 (green), -56.2 (pink), -16.5 (grey), and -12.6 (orange). The region below $S = 0$ is shaded light blue and labeled 'n-type materials' and 'p-type materials'.

Figure 1 is a scatter plot showing the activation energy (eV) of various photocatalytic materials. The y-axis represents activation energy in eV, ranging from 0 to 1.6. The x-axis is categorized by material type and preparation method: TiO_2 (blue background), Co_3O_4 (red background), and $(\text{Ti,Co})\text{O}_x$ (green background). Each category is further divided into 'as-deposited' and 'additionally annealed' states. Data points are labeled with author names and years. A red oval highlights the 'Our films' data points for $(\text{Ti,Co})\text{O}_x$, which are clustered around 0.2-0.3 eV. The TiO_2 data points are mostly below 0.4 eV, while the Co_3O_4 data points are mostly above 0.2 eV, with some outliers like [S.G. Victoria 2015] reaching up to 1.6 eV.

Material	Preparation Method	Activation Energy (eV)	Reference
TiO_2	as-deposited	~0.72	[D. Mardare 2000]
	additionally annealed	~0.08	[I. Oja 2006]
	additionally annealed	~0.08	[I. Oja 2006]
	additionally annealed	~0.25	[J. Olejnicek 2019]
	additionally annealed	~0.28	[V. Balouria 2013]
Co_3O_4	as-deposited	~0.25	[V. Balouria 2013]
	as-deposited	~0.28	[C.S. Cheng 1998]
	as-deposited	~0.28	[C.S. Cheng 1998]
	additionally annealed	~0.25	[V.R. Shinde 2005]
	additionally annealed	~0.28	[V.R. Shinde 2005]
$(\text{Ti,Co})\text{O}_x$	as-deposited	~0.25	[S. Bhat 2018]
	as-deposited	~0.28	[S. Bhat 2018]
	as-deposited	~0.28	[S. Bhat 2018]
	additionally annealed	~0.25	[S. Bhat 2018]
	additionally annealed	~0.28	[S. Bhat 2018]

Figure 12. The effect of annealing and the form of occurrence of TiO_2 , Co_3O_4 , and $(\text{Ti},\text{Co})\text{O}_x$ materials on their activation energies and comparison in relation to the films prepared by the authors [6,9–11,63].

The relationship between the resistivity of the thin films and temperature is depicted in Figure 13a. For each thin film, regardless of the Co content in the (Ti,Co)O_x films, the resistivity decreased as the temperature increased, indicating the semiconducting nature of all as-deposited thin films. By analyzing the slope of $\log(\rho)$ as a function of $1000/T$, the thermal activation energies (E_a) were determined using the exponential Arrhenius formula. The experimental results exhibited an excellent fit with a single straight line, indicating a predominant thermally activated mechanism of electrical conduction. Figure 13b illustrates the relationship between the cobalt content in the films and their activation energy values. The activation energy ranged from 0.0058 eV to 0.267 eV, with the highest value observed for thin films containing 3 at.% of Co.

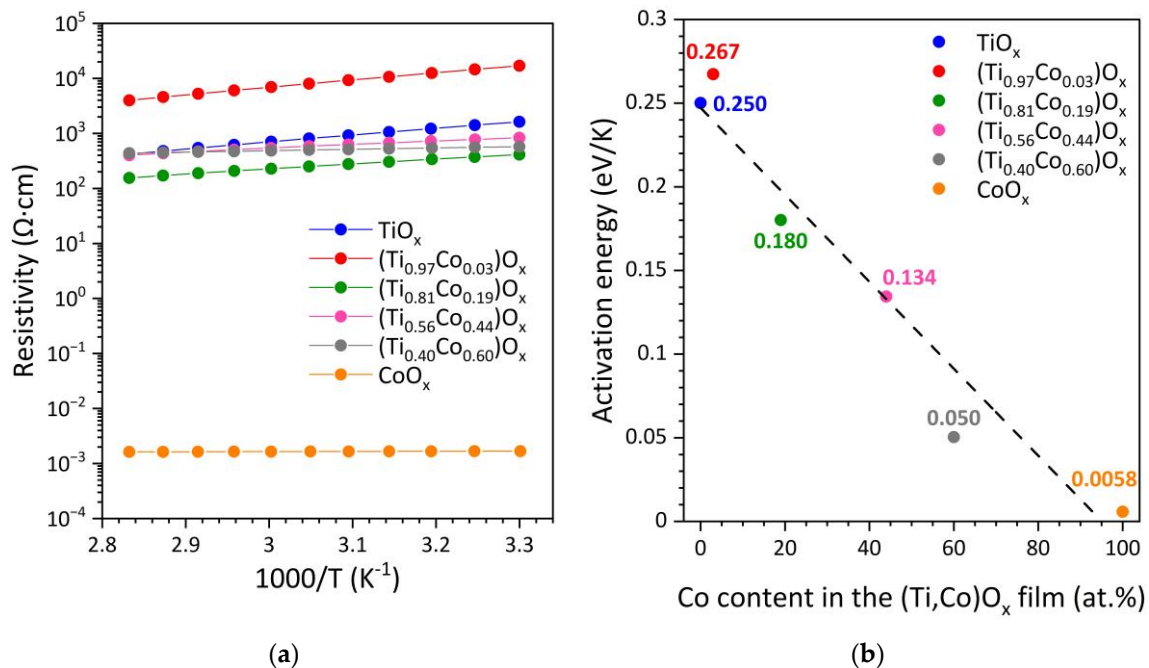


Figure 13. (a) Temperature-dependent resistivity and (b) activation energy of (Ti,Co)O_x films.

4. Conclusions

This study focused on the preparation and comprehensive characterization of non-stoichiometric (Ti,Co)O_x thin films, prepared by the Gas Impulse Magnetron Sputtering (GIMS) technique. The films were systematically evaluated to understand their material composition, microstructure, and electrical properties, with varying Co content, ranging from 3 at.% to 60 at.%. Atomic Force Microscopy (AFM) and optical profiling techniques revealed that the films had smooth, crack-free surfaces with remarkable homogeneity. The root mean square surface roughness (RMS) values decreased with increasing Co content in the films, suggesting an impact on the film's microstructure. The films exhibited ohmic behavior with linear current-voltage (I-V) characteristics. The resistivity of the films showed substantial variations, ranging from approximately 10^{-3} to 10^4 $\Omega\cdot\text{cm}$. Notably, as the Co content in the films increased, the resistivity values successively decreased. This correlation between Co content and electrical conductivity is a significant finding, indicating potential applications in semiconductor technology. Thermoelectric measurements revealed that all the films exhibited weak n-type semiconducting properties, as indicated by the Seebeck coefficients (S) decreasing to zero. The films' resistivity decreased with increasing temperature, affirming their semiconducting nature. Activation energy (E_a) values ranged from 0.0058 eV to 0.267 eV, with the highest E_a observed for films containing 3 at.% Co (Figure 14). The findings offer valuable insights into the potential application of these films in semiconductor technology and materials science. The correlation between Co content and electrical conductivity suggests avenues for tailored material design, with potential

implications in various electronic and optoelectronic applications. Further research can explore the optimization of these films for specific use cases, potentially unlocking new opportunities in materials engineering and device development, e.g., for electronics.

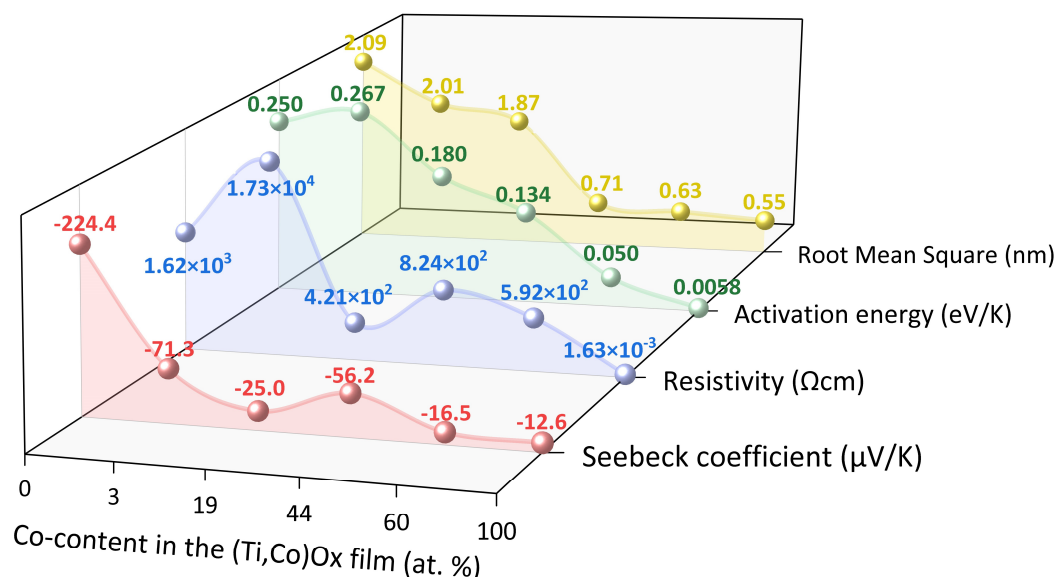


Figure 14. Influence of Co content in non-stoichiometric (Ti,Co)O_x thin films on their various surface and electrical parameters.

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