



# Article Chemiresistors Based on Li-Doped CuO–TiO<sub>2</sub> Films

Alfio Torrisi <sup>1,2,\*</sup>, Jiří Vacík <sup>1</sup>, Giovanni Ceccio <sup>1</sup>, Antonino Cannavò <sup>1</sup>, Vasily Lavrentiev <sup>1</sup>, Pavel Horák <sup>1</sup>, Roman Yatskiv <sup>3</sup>, Jan Vaniš <sup>3</sup>, Jan Grym <sup>3</sup>, Ladislav Fišer <sup>4</sup>, Martin Hruška <sup>4</sup>, Přemysl Fitl <sup>4</sup>, Jaroslav Otta <sup>4</sup> and Martin Vrňata <sup>4</sup>

- <sup>1</sup> Nuclear Physics Institute (NPI) of CAS, 250 68 Husinec-Řež, Czech Republic; vacik@ujf.cas.cz (J.V.); ceccio@ujf.cas.cz (G.C.); cannavo@ujf.cas.cz (A.C.); lavrentiev@ujf.cas.cz (V.L.); phorak@ujf.cas.cz (P.H.)
- <sup>2</sup> Department of Mathematics and Physics "Ennio de Giorgi" & CEnter of Applied Physics, DAting and Diagnostics (CEDAD)—University of Salento, 73 100 Lecce, Italy
- <sup>3</sup> Institute of Photonics and Electronics (IPE) of CAS, 182 51 Prague, Czech Republic; yatskiv@ufe.cz (R.Y.); vanis@ufe.cz (J.V.); grym@ufe.cz (J.G.)
- <sup>4</sup> Department of Physics and Measurements, Faculty of Chemical Engineering, University of Chemistry and Technology Prague (UCT), 166 28 Prague, Czech Republic; Ladislav.Fiser@vscht.cz (L.F.); Martin1.Hruska@vscht.cz (M.H.); premysl.fitl@vscht.cz (P.F.); Jaroslav.Otta@vscht.cz (J.O.); martin.vrnata@vscht.cz (M.V.)
- \* Correspondence: torrisi@ujf.cas.cz

**Abstract:** Chemiresistors based on thin films of the Li-doped CuO–TiO<sub>2</sub> heterojunctions were synthesized by a 2-step method: (i) repeated ion beam sputtering of the building elements (on the Si substrates and multisensor platforms); and (ii) thermal annealing in flowing air. The structure and composition of the films were analyzed by several methods: Rutherford Backscattering (RBS), Neutron Depth Profiling (NDP), Secondary Ion Mass Spectrometry (SIMS), and Atomic Force Microscopy (AFM), and their sensitivity to gaseous analytes was evaluated using a specific lab-made device operating in a continuous gas flow mode. The obtained results showed that the Li doping significantly increased the sensitivity of the sensors to oxidizing gases, such as NO<sub>2</sub>, O<sub>3</sub>, and Cl<sub>2</sub>, but not to reducing H<sub>2</sub>. The sensing response of the CuO–TiO<sub>2</sub>–Li chemiresistors improved with increasing Li content. For the best sensors with about 15% Li atoms, the detection limits were as follows: NO<sub>2</sub>  $\rightarrow$  0.5 ppm, O<sub>3</sub>  $\rightarrow$  10 ppb, and Cl<sub>2</sub>  $\rightarrow$  0.1 ppm. The Li-doped sensors showed excellent sensing performance at a lower operating temperature (200 °C); however, even though their response time was only a few minutes, their recovery was slow (up to a few hours) and incomplete.

Keywords: chemiresistor; CuO-TiO<sub>2</sub> heterojunction; Li-doping

# 1. Introduction

The CuO–TiO<sub>2</sub> heterogeneous films with a p–n heterojunction have attracted the attention of the scientific community as promising materials with a high application potential in gas sensing [1–5], and also in technologies of semiconductor photocatalysis [6,7] or lithium-ion batteries [8]. The advantages of using a two-metal-oxide compound lie in its nontoxicity, chemical stability, low market price, and high absorption coefficients [9]. Specifically, for the gas sensing, CuO–TiO<sub>2</sub> combines the distinct advantages of the first CuO monometallic oxide, such as a low bandgap [10], with the high reactivity of the second TiO<sub>2</sub> monometallic counterpart [11]. Various physical and chemical methods have been used for the synthesis of the CuO–TiO<sub>2</sub> systems prepared in different forms (as nanocomposite alloys or thin multilayered films), e.g., chemical vapor deposition [12], a combination of electrospinning and hydrothermal processes [13], magnetron sputtering [14], thermal evaporation and oxidation [15], and some other techniques [16]. Furthermore, it has been shown that the performance of the chemiresistive gas sensors can also be directly influenced in several other ways, for instance, by a proper morphology of the semiconductor oxide films (including zero-dimensional to three-dimensional structures) [17]; surface modification,



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). which can be tunable for specific applications [18]; and also by doping (incorporation) with certain species (alkali or noble metals), such as gas sensors combined with Au [19] and Pt nanoparticles, improving the charge carrier separation, with beneficial effects on sensitivity response time and operational temperature [20,21]. In this work, we have used a combined method consisting of low-energy Ar<sup>+</sup> ion beam sputtering (IBS) and subsequent thermal annealing in air.

Nitrogen dioxide (NO<sub>2</sub>) represents an oxidizing corrosive gas that is potentially dangerous for humans even at relatively low concentrations. It is particularly urgent to develop high-performance sensors with a fast selectivity and response. Another oxidizing gas widely used in technologies is ozone (O<sub>3</sub>) [22,23], which can also be dangerous; therefore, it is necessary to monitor its concentration in the surrounding atmosphere. Chlorine (Cl<sub>2</sub>) also represents a hazardous gas that can affect the human body in various ways, such as causing skin infections or liver tumors [24,25].

So far, several types of semiconductor metal-oxide sensors for the detection and monitoring of NO<sub>2</sub>, O<sub>3</sub>, and Cl<sub>2</sub> gases have been proposed [26,27]. Their common sensing mechanism is based on the change in the electrical conductivity during the adsorption/desorption of the gas molecules on the sensitive films. However, mono-metal-oxide sensors usually do not exhibit superior gas selectivity and require high temperatures for maintenance (e.g., rapid desorption of the adsorbed molecules). On the other hand, as has been confirmed [9,13], the performance of the sensors can be greatly enhanced using heterogeneous nanomaterials, where p- and n-type metal oxides are combined and form efficient p-to-n transition sensing chemiresistors. In this class of sensors, the n-p heterojunctions are based on the electrical contact of the n-type (e.g., SnO<sub>2</sub>, TiO<sub>2</sub>, WO<sub>3</sub>, MoO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, ZnO) and p-type (CuO, Co<sub>3</sub>O<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, NiO, PdO, etc) nanomaterials. A number of studies have shown that such sensors can be highly sensitive to both reducing gas (H<sub>2</sub>, H<sub>2</sub>S, CO, CH<sub>4</sub>, NH<sub>3</sub>, etc.) [28–31] as well as oxidizing gas (NO<sub>2</sub>, NO, O<sub>3</sub>, SO<sub>2</sub>, etc.) [32].

Recently, attention also has been paid to alkali metal doping, which has been confirmed to be responsible for a significant modification of the properties of heterojunctions [33]. The oxidic materials doped with lithium ions found a broad application area in batteries and energy storage, but their gas-sensing properties have only been researched in a few studies. In general, it was observed that Li has a great effect on the structure and properties of the doped materials. For instance, a strong correlation was confirmed between the lithium content and (i) microstructure morphology [34], (ii) electrical parameters (resistivity, bandgap, and electrical stability [35], and (iii) optical properties [34,35] of metal oxides. Interestingly, it was observed that lithium tends to occupy the structural defects, and it tends to segregate and accumulate with higher concentrations on the surface of the metal oxide films [36]. The high diffusivity and interactivity of lithium make it possible, in principle, to modify the electrical properties of nanostructures, which are used for gas sensors. For instance, in the work developed by Zhao et al. [37], it was demonstrated how to improve the performance of the metal oxide nanoparticles by Li doping. The presence of Li was shown to increase both the concentration of the oxygen vacancy and oxygen interstitial, which led to a higher sensitivity of the sensors.

A basic study of the sensing properties of the materials (closely related to the systems inspected in this paper), i.e., ilmenite-type cobalt titanates doped with various metal cations (2% Li, Na, K, Sb, La, Sm, Gd, Ho, and Pb), was reported in [38,39]. The authors tested the sensitivity and selectivity to ethanol vapors and propane and concluded that Li-doped cobalt titanates behave like p-type semiconductors and show the best results of all the above-mentioned cations. It was also demonstrated that CoTiO<sub>3</sub>: Li is very suitable for chemiresistors operated at relatively low temperatures of 300–450 °C. In another study, Li<sup>+</sup>-doped ZrTiO<sub>4</sub> was shown to work as an effective air humidity sensor [40]. It was found that the small addition of Li ions increases the sensitivity of the composite by two orders of magnitude; it also increases its conductivity, and enables the sensors to operate at room temperature. However, the observed improvement in sensor performance by lithium doping is not yet well understood. An attempt to interpret the enhanced gas-sensing

properties of the lithium-doped oxides is reported in [38], where, after the addition of lithium, both the conductivity and gas sensing parameters of the ZnO improved. This was explained by the particular role of the Li<sup>+</sup> ions, which stimulated the occurrence of the oxygen interstitials and vacancies that play a key role in the formation of active sites.

To the best of our knowledge, there are currently no studies on the gas-sensing performance of the heterogeneous Li-doped CuO–TiO<sub>2</sub> systems. This work, therefore, deals with the question of what effect Li has on the sensor properties of CuO–TiO<sub>2</sub> at different concentrations, and what is the driving force behind it. The sensing efficiency was tested for both oxidizing (NO<sub>2</sub>, O<sub>3</sub>, and Cl<sub>2</sub>) and reducing (H<sub>2</sub>) gases. The expectation was that this work would be a tool to shed more light on this issue.

#### 2. Materials and Methods

## 2.1. Samples Preparation

The depositions of thin multilayers based on Cu, Ti, and Li were performed by ion beam sputtering (using the Low Energy Ion Facility (LEIF) at the Center of Accelerators and Nuclear Analytical Methods (CANAM), a large scientific infrastructure at NPI [41]), employing the Cu (purity 3N5), Ti (4N), and Li (3N) as sputtering targets (MaTeck). The targets were fixed on a rotatable holder (cooled by water) and bombarded by Ar<sup>+</sup> ions with an energy of 25 keV and a current of 15  $\mu$ A. The deposition rates measured on the substrates (placed at a distance of 30 mm from the targets) were 1.62 nm min<sup>-1</sup>, 0.4 nm min<sup>-1</sup>, and 0.12 nm min<sup>-1</sup> for Cu, Ti, and Li, respectively. Diced silicon wafers (001),  $10 \times 10$  mm (Tedpella), and Multi-Sensor-Platforms KBI-2 (Tesla Blatna, CR) were employed as substrates. The sensing platform KBI-2 is a product of the Tesla Blatná, a.s. company; its datasheet can be found on [42] and its scheme is presented in Figure 1. The platform integrates an interdigitated platinum electrode structures (in Figure 1 marked as IDE), platinum resistive heating, and temperature sensor on a ceramic substrate. The heater and temperature sensor are covered with a passivating glass layer. The Cu-Ti-Li sensitive layers were deposited on the interdigitated electrode structures. Platform parameters: interdigitated electrode structures (width 15  $\mu$ m, depth 15  $\mu$ m); temperature sensor (1000  $\Omega$ at 0 °C); heater ((8.0  $\pm$  1.5)  $\Omega$  at 0 °C); and heating input (3 W at 200 °C).



**Figure 1.** Scheme of the KBI-2 sensor platform with typical dimensions in millimeters (**left**); real appearance (**right**).

The Cu and Ti components were kept fixed for each sample, as well as for their ratio (see below), varying only the relative content percentage of Li (see Table 1). The samples were prepared as multilayer systems consisting of 47 regularly alternating nanolayers of each individual sputtered element. The thickness of each nanolayer was  $\leq 1$  nm, so

the total thickness of the composites was supposed to be about 100–110 nm. In order to obtain a sufficient number of the active CuO–TiO<sub>2</sub> heterojunctions but at the same time to prevent (or reduce) the formation of the undesirable (inactive) oxidation states of the phases (especially Cu<sub>2</sub>O), it was necessary to choose the optimal annealing conditions. Because TiO<sub>2</sub> is formed at a temperature of about 400 °C [43] and CuO around 350 °C [44], an annealing temperature of 415 °C was chosen. But since Cu<sub>2</sub>O is already formed at 200–300 °C [43], it was necessary to choose short-term annealing of 1 h in order to limit the formation of unsuitable phases, and also to reduce the occurring spatial separation of the elements [45]. However, despite the short annealing time, both phases of copper oxide (cuprous oxide Cu<sub>2</sub>O and cupric oxide CuO) are expected to be formed. Thus, since it is necessary to prepare about the same amount of CuO as TiO<sub>2</sub>, the ratio between Cu and Ti had to be increased, e.g., to about 2:1 (the actual ratio, however, somewhat fluctuated, see below).

**Table 1.** Intended composition and thickness of the Cu–Ti, Cu–Ti–Li<sub>low</sub>, and Cu–Ti–Li<sub>high</sub> composites (the relative contents and thickness change after oxidation).

Sensor	Cu (at.%)	Ti (at.%)	Li (at.%)	#Nanolayers	Thickness (nm)
Cu–Ti	66.6	33.3	0	94	100
Cu-Ti-Li <sub>low</sub>	64.7	32.3	3	141	103
Cu–Ti–Li <sub>high</sub>	52.7	26.3	21	141	110

## 2.2. Samples Characterization

The composite layers were analyzed (before and after thermal annealing) by several techniques. Elemental and depth profile measurements of Ti and Cu were performed by RBS (Rutherford Backscattering Spectrometry) using 2.0 MeV alpha particles (at High Voltage Tandetron 4130 MC accelerator, NPI CANAM), and the Li content was measured by NDP technique [46,47] (Neutron Depth Profiling, CANAM) using a thermal neutron beam from the super-mirror neutron guide at the LVR15 research reactor (operated by Research Center Řež [48]). The surface morphologies of the samples were analyzed by the AFM method (NT-MDT Ltd., scanning probe microscope NTEGRA Aura). The multilayer structure of the sample and its changes (intermixing of elements and phases) were measured by the C-TOF-SIMS (compact time-of-flight of secondary ion mass spectrometry, TOFWORK AG, using the Ga<sup>+</sup> ions with the energy of 30 keV and a current of 1000 pA) operated by IPE Prague [49].

## 2.3. Measurement and Evaluation of Sensor Response

## 2.3.1. Apparatus for Measurement

The sensing properties, i.e., detection of selected gases (NO<sub>2</sub>, O<sub>3</sub>, Cl<sub>2</sub>, and H<sub>2</sub>) on the prepared heterogeneous composites, were measured in the laboratories of the UCT Prague. The methodology and equipment for measuring the sensing properties is analogous to that described in [50]. The apparatus was constructed as a continuous-flow system. Its gas distribution includes two Tedlar bags for the reference and the tested mixture, respectively; two solenoid switching valves; glass pipes; and a Teflon measuring chamber with the sensor on the KBI-2 platform. The constant flow rate of 40 mL·min<sup>-1</sup> was controlled by a rotameter (Aalborg Instruments & Controls, model P 150 mL). The dead volume of the apparatus, including its part from the solenoid switching valves to the rotameter, was ca 20 mL. The sensor resistance was measured by a multiplexer switching unit with an incorporated Agilent 34970A multimeter (the measuring voltage was set automatically but did not exceed 5 V). A multiplexing unit was used for measurement of the sensor temperature from Pt1000 thermometer incorporated on the KBI-2 platforms, and the resistance of the sensing film deposited on the interdigital electrodes.

## 2.3.2. Preparation of Gaseous Analytes

As for hydrogen (1000 ppm), nitrogen dioxide (10 ppm), and chlorine (10 ppm), the corresponding gaseous mixtures containing these analytes diluted with synthetic air were obtained from Linde Gas (Czech Republic) company. These mixtures were filled in 10 L Tedlar<sup>®</sup> sample bags (SKC, Inc.) and used for measurement as delivered. To prepare ozone (0.6 ppm), we used a generator SOG-1 (UVP). The exact concentration of produced ozone was then verified by coulometric titration.

The sensitivity was evaluated in all cases according to the following scheme: An average of the last twenty values of sensor resistance recorded before switching the atmosphere (*synthetic air*  $\rightarrow$  *gas* + *synthetic air*) was divided by an average of the last twenty values of sensor resistance recorded before reverse switching (*gas* + *synthetic air*  $\rightarrow$  *synthetic air*). The averaging was calculated in order to minimize the influence of signal noise.

## 3. Results and Discussion

The preparation of the CuO–TiO<sub>2</sub>–Li composites with active heterojunctions requires an effective homogeneous mixing of phases. In the first step of the composite synthesis (by IBS), tens of repeated multilayers (Cu/Ti/Li) are formed, which in the second step (by annealing in the flowing air) intertwine and interact with oxygen to form oxides of building elements. In this step, it is important that the formation of inappropriate oxides (e.g., Cu<sub>2</sub>O) and spatial separations of phases do not occur. Therefore, it was necessary to choose and optimize a procedure that would limit these two aspects as much as possible. In the experiment, in addition, to monitor the synthesis of mixed phases, it was also needed to control their spatial separation. For this purpose, the samples were inspected before and after annealing and for each sample with a different Li content, to assess the spatial distribution of elements and corresponding phases and to assess their effect on the sensing properties of the composites. The main results of the study, obtained by several complementary methods, are discussed below.

# 3.1. AFM Analysis

Figure 2 shows the surface morphology (measured on a scanning area of  $20 \times 20 \ \mu\text{m}^2$ ) of the composites for different Li contents before (a–c) and after (e–d) annealing. The AFM micrographs indicate significant changes in the morphology observed after annealing (due to the phase mixing), but also before annealing (after deposition, due to the incorporation of lithium). If the data are compared with the results of AFM performed on the CuO–TiO<sub>2</sub> composite prepared without the Li addition [4,5], one can point out the strong effect that lithium has on the morphology of the samples.

Depending on the increasing Li concentration, a dramatic evolution of morphology can be observed. Without Li, the surface of the sample is finely granular (with only a few signs of depressions), with densely packed nanoparticles (NPs, about 30 per  $\mu$ m<sup>2</sup>) and a low roughness  $R_{rms}^{no Li} = 3.31 \ nm$  (corresponding to a low value of the relative surface area  $S_r/S_p = 0.203\%$ , where  $S_r = 400.986 \ \mu m^2$  is a real surface area, and  $S_p = 400.173 \ \mu m^2$  a projected area, the same for all measurements). After annealing, the granular morphology with about the same NP density remains; however, the surface roughness increased by almost 70% ( $R_{rms}^{no\ Li} = 5.55\ nm$ ) and the relative surface area more than twice ( $S_r/S_p = 0.476\%$ ;  $S_r = 402.078 \ \mu m^2$ ). For the sample with a low content of Li, the surface still appears to be uniformly granular with a density of NPs of about 25 per  $\mu$ m<sup>2</sup> ( $R_{rms}^{low Li} = 4.56 nm$ , and  $S_r/S_p = 0.470\%$ ;  $S_r = 402.054 \ \mu m^2$ ). However, after annealing the growing interconnections of the NPs into planar domains of different sizes (<1  $\mu$ m) and shapes, leading to their density of about 5–10 per  $\mu$ m<sup>2</sup>, a slightly lower (~6%) surface roughness ( $R_{rms}^{low Li} = 4.29 nm$ ) was seen, and  $S_r/S_p = 0.349\%$  ( $S_r = 401.573 \ \mu m^2$ ). Samples with a high content of Li changed their granular morphology dramatically into round domains (with a chimney-like shape) with a height up to 100 nm and a density of about 5 per  $\mu$ m<sup>2</sup>, a high surface roughness  $(R_{rms}^{high Li} = 18.11 \text{ nm})$  and also  $S_r/S_p = 2.692\%$  ( $S_r = 410.947 \text{ }\mu\text{m}^2$ ). After annealing, the domains joined/coalesced and formed interconnected objects of irregular shapes, with



**Figure 2.** AFM micrographs of the Cu–Ti, Cu–Ti–Li<sub>low</sub>, and Cu–Ti–Li<sub>high</sub> composites as deposited on Si by IBS (**a**–**c**), and after annealing at 415 °C for 1 h (**d**–**f**).

The development of the surface morphology is briefly depicted in Figure 3, where a comparison of  $R_{rms}$  for samples with a different relative content of Li before and after annealing is given. As can be seen (and as mentioned above), the surface roughness remains at a similar level for the Cu–Ti–Li<sub>low</sub> sample before and after annealing. However, for the sample with a high relative content of Li (Cu–Ti–Li<sub>high</sub>),  $R_{rms}$  rises sharply both after IBS-deposition (approx. 5×), and especially after thermal annealing (approx. 10×). This is due to the effect of higher concentrations of Li on the morphology (and structure) of the heterogeneous composites. To shed more light on it, the samples were further analyzed by several profiling methods—NDP, RBS, and SIMS. It should be noted, however, that the NDP and RBS analyses were performed only for the IBS-deposited samples, because, as shown by AFM, the composites acquire a high surface roughness after annealing and are therefore not suitable for the NDP and RBS measurements. In addition, it is not expected that the total content of building elements will change after annealing; the elements will only be mixed and oxidized.

## 3.2. NDP Analysis

NDP investigations make it possible to determine the quantity of Li atoms in the samples and their concentration vs. depth. The method is based on the nuclear reaction  $(n_{th}, \alpha)$  of thermal neutrons with the <sup>6</sup>Li isotope (~7.5% abundance), which has a high cross-section  $\sigma = 940$  b and relatively high energy of reaction Q = 4782 keV. The energy spectra measured for the IBS-deposited samples with a low and high concentration of Li are shown in Figure 4. There are two pairs of peaks that correspond to the two reaction products—tritons (2727 keV, channel~1000) and alpha particles (2055 keV, channel~750)—for two samples with a low (red line) and high (black line) relative content of Li. Using the NIST standard (based on calibrated <sup>10</sup>B implanted to Si wafer), the amount of Li atoms was determined to be  $0.18 \times 10^{17}$  at./cm<sup>2</sup> and  $1.29 \times 10^{17}$  at./cm<sup>2</sup> (with about 10% uncertainty) for the Cu–Ti–Li<sub>low</sub> and Cu–Ti–Li<sub>high</sub> samples, respectively. Because the thickness of the composites was ~100 nm, NDP (with the depth resolution ~10 nm nominal) did not allow the depth profiles of lithium to be determined in sufficient detail.



**Figure 3.** Dependence of the surface roughness on the relative content of Li in the samples asdeposited (black line) and after annealing (red line).



**Figure 4.** NDP energy spectra measured for the as-prepared Cu–Ti–Li composites with a lower (red line) and higher (black line) Li content.

## 3.3. RBS Analysis

Using RBS with a 2 MeV alpha probe, it was possible to determine the elemental composition of the samples (except light particles including Li) and depth profiles of the building elements (however, since the spatial resolution is only about 10 nm, it was not possible to evaluate the profiles in high detail, similarly to NDP). In Figure 5, the RBS spectra of the IBS-deposited composites Cu–Ti (a) and Cu–Ti–Li with a low (b) and high (c) Li content are presented. The depth profiles of the building elements, including oxygen (evaluated by the SIMNRA code [51]), are shown in the insets.



**Figure 5.** RBS spectra measured for the as-deposited Cu–Ti (**a**) and Cu–Ti–Li (**b**,**c**) composites with a low (**b**) and high (**c**) Li content. The depth profiles of building elements evaluated by the SIMNRA code are presented as insets in all spectra.

Several aspects can be identified in the RBS spectra. For instance, oxygen is incorporated in a high amount in samples prepared by IBS as multilayers (i.e., before annealing in the air). Its incorporation (e.g., due to oxidation of the building elements) took place either during the preparation process (because of the residual air in the deposition chamber) or during transportation and analyses in air. The amount of oxygen increases sharply (approximately  $2\times$ ) in the sample with the high proportion of Li. This can be attributed to the oxidation of the incorporated Li. Moreover, as expected, the sample thickness increased with increasing Li content—by about 8% for the sample with a low relative content of Li (compared to the sample without Li), and 33% for the sample with a high relative content of Li (it should be noted that the increase in the sample thickness, measured by RBS, is mainly due to the oxidation, not due to incorporated Li). As can be seen in (c), besides the peaks of the building elements (except Li), also a broad Ar peak is observed in the spectrum. This is obviously due to the extensive bombardment of the targets by Ar<sup>+</sup> ions, when they are backscattered and/or entrained by sputtered atoms of building elements.

The results of the measurements with the help of RBS and NDP, presented in Table 2, shows the concentrations and relative contents of the building elements (including oxygen) in the composites after the first step of the sample preparation. In addition, information on the stoichiometric ratios and thicknesses (in  $10^{15}$  at. cm<sup>-2</sup>) of the individual samples is also given. As can be seen, the required 2:1 ratio between Cu and Ti have not been reached fully. The actual ratio varied from 2.00:1.14 for Cu–Ti via an optimal value 2.00:1.00 for Cu–Ti–Li<sub>low</sub> to 2.00:1.26 for Cu–Ti–Li<sub>high</sub>. The reason for this fluctuation can be attributed to unstable sputtering rates (due to small changes in the intensity of the Ar<sup>+</sup> beam), as well as to difficulties to maintain accurate sputtering times (it should be mentioned that sputtering takes only tens of seconds for deposition of a single nanolayer). The analysis of the data in Table 2 documents also other aspects. It turns out that Cu and Ti are not fully oxidized. If the formation of only CuO, TiO<sub>2</sub>, and Li<sub>2</sub>O phases is taken into account (although this is not

realistic), the percentage of unoxidized Cu and Ti can be derived as follows: Cu-Ti  $\rightarrow$  77% Cu and 59% Ti, Cu–Ti–Li\_{low}  $\rightarrow$  84% Cu and 68% Ti, and Cu–Ti–Li\_{high}  $\rightarrow$  64% Cu and 43% Ti. If for simplicity, it is assumed that lithium (as a highly reactive element) is fully oxidized (to Li<sub>2</sub>O) and the remaining oxygen ( $O_r$ ) is bound to Cu and Ti only, then the  $O_r/Cu+Ti$ ratio should be similar in all samples. However, the evaluation showed that this ratio fluctuates: Cu-Ti  $\rightarrow$  0.45, Cu-Ti-Li<sub>low</sub>  $\rightarrow$  0.32, and for Cu-Ti-Li<sub>high</sub>  $\rightarrow$  0.66. The reason is not clear, but it is most likely a combination of several causes, such as formation of a barrier (on the surface from oxides of building elements) against the deep penetration of air into composites, or a different surface morphology (the AFM and RBS data show that the  $O_r/Cu+Ti$  ratio is affected by the surface roughness  $R_{rms}$ ). So, oxidation concerns mainly the surface and subsurface layer, the thickness of which can be estimated from the relative ratio of the oxidized elements (provided that both CuO and  $TiO_2$  phases are formed in the same layer, which is again only a simplification). In the case of homogeneous mixing of the elements, the oxidized layers correspond to the following relative part of the thickness: Cu-Ti  $\rightarrow$  33%, Cu-Ti-Li\_{low}  $\rightarrow$  16%, and Cu-Ti-Li\_{high}  $\rightarrow$  36%. One can see that Cu–Ti–Li<sub>high</sub> is the most oxidized sample, which can be due to its surface morphology with chimney NPs (Figure 2c) that enlarge the surface area. Cu-Ti-Li<sub>low</sub>, on the other hand, is the least oxidized, which is probably because the sample contains the highest amount of Cu, which does not undergo as intense oxidation as Ti. As mentioned above, the total thickness of the composites is different—it changes (grows) with Li (and its oxidation). The contribution (in  $10^{15}$  at. cm<sup>-2</sup>) by only Cu and Ti is nearly identical for all samples: Cu-Ti  $\rightarrow$  4.14, Cu-Ti-Li<sub>low</sub>  $\rightarrow$  4.88, and Cu-Ti-Li<sub>high</sub>  $\rightarrow$  4.14 (a higher value for Cu-Ti-Li<sub>low</sub> is due to a higher amount of Cu). The other contributions are (i) due to oxidation of Cu and Ti (Cu-Ti  $\rightarrow$  1.86, Cu-Ti-Li<sub>low</sub>  $\rightarrow$  1.54, and Cu-Ti-Li<sub>high</sub>  $\rightarrow$  2.71), and (ii) incorporated Li and its oxidation (Cu-Ti-Li<sub>low</sub>  $\rightarrow$  0.27, Cu-Ti-Li<sub>high</sub>  $\rightarrow$  1.94).

**Table 2.** Concentration, relative content, and stoichiometric ratio of the Cu, Ti, O, and Li elements in the as-deposited thin-film composites. The thickness (in  $10^{15}$  cm<sup>-2</sup>) was obtained from both NDP and RBS measurements.

Phase Elements	Concentration (10 <sup>17</sup> cm <sup>-2</sup> )	Relative Content Including Oxygen (%)	Relative Content without Oxygen (%)	Stoichiometric Ratio	Thickness (10 <sup>15</sup> cm <sup>-2</sup> )
Cu–Ti					
Cu	2.64	44	63.8	$C_{\rm res}/{\rm T}_{\rm r}^{\rm s}/{\rm O}$	
Ti	1.50	25	36.2	Cu/11/O	6.00
О	1.86	31	-	1/0.36/0.71	
Cu-Ti-Li <sub>low</sub>					
Cu	3.25	48.5	64.2		
Ti	1.63	24.4	32.2	Cu/Ti/O/Li	( (0
0	1.63	24.4	-	1/0.50/0.50/0.05	6.69
Li	0.18	2.7	3.6		
Cu-Ti-Li <sub>high</sub>					
Cu	2.54	28.9	46.8		
Ti	1.60	18.2	29.5	Cu/Ti/O/Li	0.70
0	3.36	38.2	-	1/0.63/1.32/0.51	8.79
Li	1.29	14.7	23.7		

#### 3.4. TOF-SIMS Analysis

TOF-SIMS analysis allowed us to monitor the distribution of the building elements in the samples before and after thermal annealing both in the cross section and on the surface (the latter case is not presented here). The SIMS data significantly complement the measurements by NDP and RBS and bring forth information on the distribution of the elements with a  $39 \times 39$  nm spatial resolution.

Figure 6 shows cross sections of the SIMS stack frames and corresponding sputtering profiles (of the <sup>48</sup>Ti and <sup>63</sup>Cu<sup>48</sup>Ti<sup>16</sup>O ions) obtained for the Cu–Ti sample before (a) and after (b) annealing. Both the x-axis (frontal) and y-axis (perpendicular to the plane with

an integrated signal) in the images are set to 20  $\mu$ m; the z-axis (from top to bottom) is constructed by the frames, with an initial 0 frame at the surface. The color represents the counting intensity, with red as the highest (the maximum is, however, different for each image) and blue as the lowest (with zero counts). The analysis showed that before annealing, the building elements were homogeneously (on a few nm depth scales) distributed, with higher oxidation only in a subsurface layer to a depth of up to about 1/3 of the total film thickness (a), which corresponds to the RBS data (see above). However, the 1-h annealing at 415 °C led to a significant redistribution of elements (b), to the transfer of Cu to a subsurface layer (representing about 20% of the total film thickness), and, consequently, to a higher abundance of Ti (with a relatively uniform distribution reaching the substrate) below it. In a somewhat wider zone (about 1/3 of the total film thickness), Cu and Ti oxides (presumably CuO–TiO<sub>2</sub>) were formed with some increase at the Cu/Ti interface. Interestingly, the distribution of the Ti and Cu oxides differs, which is perhaps due to the formation of the top Cu layer and its weaker oxidation.



**Figure 6.** Cross section of the stacked frames and sputtering profiles (in counts/frame) of the  ${}^{48}\text{Ti}^+$  and  ${}^{63}\text{Cu}{}^{48}\text{Ti}{}^{16}\text{O}^-$  ions obtained by TOF-SIMS for the Cu–Ti sample before (**a**) and after (**b**) annealing (at 415 °C for 1 h).

Figures 7 and 8 show the cross sections of the stack frames and corresponding sputtering profiles of the <sup>7</sup>Li, <sup>48</sup>Ti, and <sup>63</sup>Cu<sup>48</sup>Ti<sup>16</sup>O ions in the Cu–Ti–Li<sub>low</sub> (6) and Cu–Ti–Li<sub>high</sub> (7) samples before (a) and after (b) annealing. In Cu–Ti–Li<sub>low</sub>, the distribution of the Cu and Ti before annealing is similar as in the Cu–Ti sample, with the oxidized surface layer  $(^{63}Cu^{48}Ti^{16}O)$  being only about 15% of the total film thickness (in agreement with RBS). Li is relatively homogeneously distributed in the sample, but unlike Ti, it shows a sharp increase in the subsurface layer (with about 15% of the total film thickness), and also some increase at the interface with the Si substrate. The redistribution of Li in the films may indicate that the sample was heated during preparation (perhaps due to the deposition of sputtered atoms with a keV energy) to temperatures where Li can diffuse rapidly [52]. After annealing, Cu and Ti show similar behavior as in the Cu–Ti sample, i.e., Cu moves towards the surface and forms a subsurface layer (of about 20% of the total film thickness), while Ti is broadly distributed throughout the depth of the film below the Cu-rich layer, with a moderate decrease in concentration towards the Si substrate. The layer of both (Cu and Ti) oxides (<sup>63</sup>Cu<sup>48</sup>Ti<sup>16</sup>O) is in the form of a wide distribution partially located in the top Cu layer and Ti underlayer with a maximum at the Cu/Ti interface. The Ti oxides

(<sup>48</sup>Ti<sup>16</sup>O) form a broad distribution that begins below the Cu/Ti interface and also gradually decreases towards Si. The behavior of Li is interesting—it moves from the top layer towards the Cu/Ti interface (and is replaced by Cu), where it forms a wide distribution, reaching up to half the thickness of the sample. The rapid growth of Li was also indicated at the interface with Si, with apparent diffusion to the substrate.



**Figure 7.** Cross section of the stacked frames and sputtering profiles of the  $^{7}\text{Li}^{+}$ ,  $^{48}\text{Ti}^{+}$ , and  $^{63}\text{Cu}^{48}\text{Ti}^{16}\text{O}^{-}$  ions obtained by TOF-SIMS for the Cu–Ti–Li<sub>low</sub> sample before (**a**) and after (**b**) annealing.



**Figure 8.** Cross section of the stacked frames and sputtering profiles of the  $^{7}\text{Li}^{+}$ ,  $^{48}\text{Ti}^{+}$ , and  $^{63}\text{Cu}^{48}\text{Ti}^{16}\text{O}^{-}$  ions obtained by TOF-SIMS for the Cu–Ti–Li<sub>high</sub> sample before (**a**) and after (**b**) annealing.

Figure 8a shows that the distribution of the elements in Cu–Ti–Li<sub>high</sub> differs from the previous samples. Ti is strongly depleted in the subsurface layer (representing about 20% of the total film thickness) and forms a broad (largely homogeneous) distribution below it, which extends to the Si substrate. A similar distribution can also be assumed

for Cu. Interestingly, only relatively weak oxidation of both Ti and Cu (<sup>63</sup>Cu<sup>48</sup>Ti<sup>16</sup>O) is recorded, and (similarly as <sup>48</sup>Ti<sup>16</sup>O) it is mainly in the Ti distribution region, not in the top layer, and can be estimated to be at about 40% of the total film thickness. This is probably due to a large amount of Li on the surface, which is oxidized preferentially (as a strong reducing agent) and forms a surface barrier that prevents deep oxidizing of the sample. The results are consistent with the RBS and NDP measurements. During the deposition, lithium moves in large quantities to the surface and towards the substrate, where it forms, surprisingly, two peaks (one at the interface with Si, the other just above with a significant drop between). The reason for this bifurcation is not entirely clear, but as follows from the analysis in Figure 7 (before and after annealing), Li accumulates mainly at the boundaries between the different environments, e.g., at the surface, at the interface with the substrate, or the interface between Cu and Ti. Thus, the observed bifurcation can be considered as a manifestation of the separation of elements, when under certain conditions (e.g., at elevated temperatures and specific densities of Li, Cu, and Ti) mixed components separate from each other, i.e., when Cu separates from Ti (and accumulates above Ti) and Li separates from both Cu and Ti (and accumulates between them, below Cu and above Ti). Thermal annealing significantly changes the distribution of all building elements (Figure 8b). Ti forms a wide distribution from the surface to the substrate with a slow increase near the surface and a decrease near the interface with the Si substrate. Cu apparently moves towards the surface, where it forms a Cu-rich layer. Both Cu and Ti oxides (<sup>63</sup>Cu<sup>48</sup>Ti<sup>16</sup>O) are synthesized in the whole sample, but particularly in the subsurface layer (with a width of about 1/3 of the total film thickness). Ti oxides (<sup>48</sup>Ti<sup>16</sup>O) roughly copy the distribution of Ti.

## 3.5. Sensing Properties of the Prepared Films

The sensitivity of the heterogeneous gas sensors prepared by deposition and annealing of thin Cu–Ti, Cu–Ti–Li<sub>low</sub>, and Cu–Ti–Li<sub>high</sub> composites on the multisensor platform KBI-2 (equipped with interdigital electrodes) was tested for different oxidizing gases (NO<sub>2</sub>, O<sub>3</sub>, and Cl<sub>2</sub>) and one reducing (H<sub>2</sub>) gas. The sensors' resistance was measured at a temperature 200 °C (NO<sub>2</sub>, O<sub>3</sub>, and Cl<sub>2</sub>) or 300 °C (H<sub>2</sub>) in 'pure' synthetic air (which was used as a reference), and in synthetic air with a mixture of the oxidizing and reducing gases—10 ppm of nitrogen dioxide, 10 ppm of chlorine, 0.6 ppm of ozone, and 1000 ppm of hydrogen. The measurement was performed in a cell with a controlled gas inlet.

Figures 9–11 show the responses (i.e., the dependence of the transient resistance on time with a gas inlet window) of the Cu–Ti (a), Cu–Ti–Li<sub>low</sub> (b), and Cu–Ti–Li<sub>high</sub> (c) sensors to the oxidizing gases NO<sub>2</sub> (Figure 9), O<sub>3</sub> (Figure 10), and Cl<sub>2</sub> (Figure 11) diluted in synthetic air (response to the reducing H<sub>2</sub> gas was insignificant and hence the corresponding graph is not reported here). In Table 3, the relative sensitivities of the sensors, i.e., ratios of their transient resistance measured in oxidizing (and reducing) gases to the resistance measured in the reference synthetic air, are given.

Sensor	Baseline R <sub>air</sub> (Ω) Synthetic Air At 200 °C	Sensitivity $S = R_{NO2}/R_{air}$ $NO_2$ 10 ppm at 200 °C	Sensitivity S = R <sub>O3</sub> /R <sub>air</sub> O <sub>3</sub> 0.6 ppm at 200 °C	Sensitivity S = R <sub>Cl2</sub> /R <sub>air</sub> Cl <sub>2</sub> 10 ppm at 200 °C	Sensitivity S = R <sub>H2</sub> /R <sub>air</sub> H <sub>2</sub> 1000 ppm at 300 °C
Cu–Ti	$2.4 imes 10^4$	1.33	3.3	3.2	1.11
Cu-Ti-Li <sub>low</sub>	$1.5 imes 10^4$	3.0	30	12	no response
Cu-Ti-Li <sub>high</sub>	$6.0  imes 10^5$	6.0	120	65	1.16

Table 3. Sensitivity of the sensors to oxidizing and reducing gases measured at 200 °C (NO<sub>2</sub>, O<sub>3</sub>, and Cl<sub>2</sub>) or 300 °C (H<sub>2</sub>).



Figure 9. Response (resistance vs. time) of the Cu–Ti (a), Cu–Ti–Li<sub>low</sub> (b), and Cu–Ti–Li<sub>high</sub> (c) sensors to 10 ppm of  $NO_2$ .



**Figure 10.** Response (resistance vs. time) of the Cu–Ti (a), Cu–Ti–Li<sub>low</sub> (b), and Cu–Ti–Li<sub>high</sub> (c) sensors to 0.6 ppm of  $O_3$ .



**Figure 11.** Response (resistance vs. time) of the Cu–Ti (**a**), Cu–Ti–Li<sub>low</sub> (**b**), and Cu–Ti–Li<sub>high</sub> (**c**) sensors to 10 ppm of Cl<sub>2</sub>.

## 3.5.1. NO<sub>2</sub> Response

It turned out that the active parts (heterojunctions) of the sensors strongly react to the diluted NO<sub>2</sub> (and also to O<sub>3</sub> and Cl<sub>2</sub>) as a semiconductor with p-type conductivity. This results from measuring the dependence of the resistance on the temperature (the resistance was increasing with decreasing temperature, as can be observed from the red lines) and from the response parameters (resistance decrease) in the oxidizing gases shown in Figures 9–11. As can be seen (in Figure 9 and Table 3), lithium significantly improves the sensitivity of the sensors to 10 ppm nitrogen dioxide, and it is proportional to the Li content (the sensitivity, quantified as  $R_{NO2}/R_{air}$ , increases with the content of Li in the sensors). Figure 9 shows the change in resistance in the time window when the gas inlet is opened and closed (indicated as ON/OFF, see the green lines). It turns out that the rate of reaction to the presence of gas is relatively fast for all sensors, i.e., in a few minutes (although with Cu–Ti–Li<sub>low</sub> the saturation of the minimum is reached after about an hour). On the other hand, while the process of recovery for the sensor without Li is rather quick (lasting for about 25 min), for the sensors with Li it is quite slow (hours) and the recovery is only partial (the sensitivity decreases by tens of percent).

## 3.5.2. O<sub>3</sub> Response

Figure 10 shows the response of the sensors to 0.6 ppm of ozone. Surprisingly, the response of Cu–Ti is relatively slow (compared to the sensors with Li) and does not reach saturation (minimum of resistance) even after an hour (for sensors with Li, saturation is reached within a few tens of minutes). As with NO<sub>2</sub>, the sensitivity of the sensors with Li to O<sub>3</sub> is significantly higher and increases with the Li content (Table 3). However, the recovery is relatively slow for all sensors (an hour for Cu–Ti and a few hours for Cu–Ti–Li<sub>low</sub> and Cu–Ti–Li<sub>high</sub>); in addition, for the sensors with Li, it is incomplete (the sensitivity decreases by several tens of percent).

## 3.5.3. Cl<sub>2</sub> Response

Figure 11 shows the response of the sensors to 10 ppm chlorine. In all cases, the sensors react very strongly (with a significant decrease of resistance) and quickly (in a few minutes). In this case, it also turns out that the higher the Li content, the stronger the response of the sensor (Table 3). For Cl<sub>2</sub>, however, the recovery is slow for all sensors (hours), and incomplete (the sensitivity decreases by about 20% for Cu–Ti, and 45% for Cu–Ti–Li<sub>low</sub> and Cu–Ti–Li<sub>high</sub>).

For comparison with the data obtained in this work, Table 4 shows some published results related to sensing performance of the CuO–TiO<sub>2</sub> sensors tested in various oxidizing and reducing gases. The sensitivity *S* was calculated as the ratio of  $R_{gas}/R_{air}$ . As can be seen, the results of sensing of CuO–TiO<sub>2</sub> in an NO<sub>2</sub> and H<sub>2</sub> atmosphere (although at different concentrations, as we used in this work) are similar to our experimental values.

CuO/TiO <sub>2</sub> Sensors	Gas	Operating Temperature (°C)	Concentration (ppm)	Gas Response (%)	Ref.
	NO <sub>2</sub>	150	20	1.20	[16]
	H <sub>2</sub>	300	125	1.50	[14]
	CO	250	50	2.77	[53]
	$H_2S$	RT	50	1.77	[54]
	C <sub>2</sub> H <sub>5</sub> OH	RT	50	35	[55]
	$C_3H_6O$	240	50	<4	[13]
	$C_6H_{15}N$	160	5	12.7	[56]

**Table 4.** Published data on the sensitivity of CuO–TiO<sub>2</sub>-based sensors to various oxidizing and reducing gases measured at different temperatures.

Table 5 shows the evaluated detection limits of the sensors for the oxidizing gases  $NO_2$ ,  $O_3$ , and  $Cl_2$  at the selected operating temperature of 200 °C. Several important aspects can be seen:

- The sensors with Li are very sensitive to all tested oxidizing gases; the sensitivity
  is higher for sensors with a higher Li content; in contrast, the sensor without Li is
  significantly less sensitive to oxidizing gases.
- The sensors do not show selectivity for oxidizing gases.
- For nitrogen dioxide, the detection limit is around ppm or a fraction thereof, which is several times higher than the recommended odor threshold concentration of 0.1–0.4 ppm [57].
- For chlorine, an odor threshold of 0.2–0.4 ppm has been acknowledged [58], which corresponds to the sensitivity of the lithium-doped sensors.
- For ozone, the detection limits of lithium-doped sensors are similar to or better than the ozone odor threshold of 0.01–0.02 ppm [59].

**Table 5.** Detections limits of the sensors for the oxidizing gases NO<sub>2</sub>, O<sub>3</sub>, and Cl<sub>2</sub> analyzed at a temperature of 200  $^{\circ}$ C.

Sensor Composition	Detection Limit NO <sub>2</sub> At 200 °C	Detection Limit O <sub>3</sub> At 200 °C	Detection Limit Cl <sub>2</sub> At 200 °C
Cu–Ti	1.0 ppm	100 ppb	1.0 ppm
Cu–Ti–Li <sub>low</sub>	0.5 ppm	20 ppb	0.5 ppm
Cu–Ti–Li <sub>high</sub>	0.5 ppm	10 ppb	0.1 ppm

Thus, one can state that the detection limits of the Cu–Ti–Li<sub>low</sub> and Cu–Ti–Li<sub>high</sub> sensors prepared so far without the optimizing Li content and sensor structure are promising to detect the hazardous gases  $O_3$  and  $Cl_2$ , and somewhat less  $NO_2$ . It can be assumed that their sensitivity and response parameters can be further improved.

The results of the experiments show that lithium in the heterogeneous Cu–Ti systems significantly increases the sensitivity of the sensors to oxidizing hazardous gases. According to Table 3, the sensitivity of Cu–Ti–Li<sub>high</sub> compared to Cu–Ti–Li<sub>low</sub> is several times higher—twice for NO<sub>2</sub>, four times for O<sub>3</sub>, and more than five times for Cl<sub>2</sub>. The ratio of the Li content in Cu–Ti–Li<sub>high</sub> and Cu–Ti–Li<sub>low</sub> (based on the NDP analysis, Table 2) is about 7.17. This raises the question concerning what is the cause of the increase in sensitivity of the sensors when Li is incorporated into their structure. According to the TOF-SIMS measurements, it turns out that the depth distribution of the building elements in the sensors (especially after annealing) is very inconsistent. There are areas that indicate a separation of the elements, e.g., the Cu-rich zone at the surface, which either overlap or mix with the Li-rich zone, under which the Ti-rich zone is formed. CuO–TiO<sub>2</sub> heterojunctions are dispersed in these areas, but also form a band below the surface (at a depth of about 15–20% of the total film thickness); the closest to the surface is the band in Cu–Ti–Li<sub>high</sub> (Figure 8b).

It is not clear whether Li (resp. lithium oxide) participates in any gas-sensing process as does the active Cu and Ti oxides. However, it is conceivable that this element with high diffusivity and immiscibility in binary systems (copper and lithium show no alloying and chemical intermixing under normal circumstances) affects the structure, elemental and phase separation, and surface morphology. It acts as an agent that to some extent, according to a greater or lesser content, shapes the structure of the composites and their surfaces. Additionally, since the performance of the sensors also depends on the surface properties [17], it can be suggested that Li acts on the properties of the sensors through the surface morphology. It is important for the sensors that the band of the active phases (i.e., heterojunctions, where the interaction of the target gas molecules with the metal oxide phases takes place) is exposed as much as possible to the detected gas, i.e., that its area is as large as possible and closest to the surface. Moreover, this phenomenon is related to the surface morphology—with great roughness, the real surface area increases, and thus also the dimensions of the active phase band. As mentioned above in the AFM study, the real area of the sensors increases with the amount of Li: for Cu-Ti-Li<sub>hieh</sub>; the real area is more than 6% larger than Cu–Ti–Li<sub>low</sub>. This can be related to the increase in the sensitivity of the sensors. The comparison of sensitivity and real surface areas of Cu–Ti and Cu–Ti–Li<sub>low</sub> is special. It turns out that the roughness (and real area) of the surface is greater in Cu-Ti, but the sensitivity to the tested gases is lower. This is surprising, but it may be due to the smaller number of heterojunctions formed in the Cu–Ti–Li<sub>low</sub> sensor, as evidenced by the RBS analysis (in Cu-Ti-Li<sub>low</sub>, relatively less oxidized Cu and Ti atoms were recorded due to the strong Cu barrier formed on the sample surface).

There is also an issue of a slower recovery time of the Li-doped sensors. It can be assumed that when the molecules of the aggressive gas penetrate towards the active centers below the surface, some interactions with Li (but also with unbound Cu and Ti) will occur, which may lead to the formation of other compounds (e.g., lithium nitride, copper oxide, titanium oxide, lithium chloride, etc.), blocking and restricting the access of the tested gases (including synthetic air). The removal of these parasitic components from the sensor structure is slow, leading to the observed phenomena of several-hour-lasting and incomplete recovery.

Thus, one can conclude that the sensitivity of the sensors based on Cu, Ti, and Li (supplemented with oxygen after annealing in the air) is strongly influenced by (i) the number of heterojunctions (the more heterojunctions are created, the greater the sensor sensitivity); and (ii) their depth distribution (the closer the heterojunctions are to the surface, the greater the sensitivity of the sensor). When creating the sensors, several factors play their (even opposite) roles. The number of heterojunctions depends on the efficiency of the oxidation process, i.e., the creation of suitable thermal conditions, which, however, should not allow the formation of the unwanted, inactive phases; however, they also arise when creating heterojunctions. The formation of zones of heterojunctions near the surface is linked to the limitation of the process of separation of the elements, which, however, takes

place in the conditions necessary for the oxidation of the Cu and Ti elements. Lithium seems to play an interesting, positive role—it diffuses towards the surface during deposition and annealing, thus limiting the formation of the Cu surface barrier (which otherwise would prevent oxidation of the lower layers). In addition, it has a strong effect on the surface morphology, which can significantly affect the sensitivity of the sensors (the greater the roughness of the surface, the larger its real area, which allows better access of the gas to the active phases, which results in higher sensitivity of the sensors). The construction of optimal Li-doped heterogeneous sensors thus requires a suitable strategy that should assess the mentioned roles, thus effectively reducing their negative aspects. However, this will require further detailed research.

## 4. Conclusions

Heterogeneous gas sensors based on CuO–TiO<sub>2</sub> composites doped with a low and high relative content of Li were tested in several oxidizing gases (NO<sub>2</sub>, O<sub>3</sub>, and Cl<sub>2</sub>), as well as reducing hydrogen H<sub>2</sub>. The thin film samples were prepared in two steps—by ion beam sputtering of high purity Cu, Ti, and Li targets and by thermal annealing in air. The composition and elemental depth profiling were analyzed by nuclear analytical methods, namely, NDP, RBS, and TOF-SIMS, and the surface morphology by scanning probe microscopy—AFM. The response (measured as the transient resistance) of the sensors to oxidizing and reducing gases was monitored in a flow cell with a controlled inlet of the tested gases (diluted in synthetic air).

The results showed that the CuO–TiO<sub>2</sub>-based chemiresistors are promising for the detection of NO<sub>2</sub>, O<sub>3</sub>, and Cl<sub>2</sub>. Although they form a complex structure, they are very sensitive and can operate even at a relatively low temperature (200 °C), exhibiting a p-type conductivity. It was demonstrated that doping with lithium significantly increases the sensing efficiency of the sensors; the best improvement was indicated for the sensor with the highest Li content. The reason is attributed to the influence of lithium on the surface morphology, which affects the sensitivity of the sensors. The additional tests performed with the reducing gas showed that the sensors are not sensitive to H<sub>2</sub>; they show only a poor or negligible response.

The first experiments with the heterogeneous sensors  $CuO-TiO_2$  doped with Li yielded promising results. It is, therefore, appropriate to perform further investigations and monitor the behavior of the optimized sensors with incorporated Li in different oxidizing and reducing environments.

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