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# Effect of deposition rate and substrate microstructure on gas sensitivity of Te thin films

## ABSTRACT

*Tellurium thin films have been prepared using different rates (0.1 ÷ 30 nm/s) by physical deposition in vacuum on glassy, sintered alumina and electrochemically nanostructured $Al_2O_3$ substrates. The sensitivity to nitrogen dioxide of fabricated films was tested at room temperature. It is shown that the deposition rate strongly influences the microstructure of the films in question, as well as their gas sensing properties. The increasing of deposition rate results in transformation of microcrystalline structure of the film into an amorphous one. Simultaneously, both the gas - sensitivity and the response time decrease. The results are explained in terms of interaction between gas molecule and lone – pair electrons of tellurium atoms.*

***Keywords:*** *deposition rate, gas sensitivity, response time, substrate, thin film.*

## 1. INTRODUCTION

Tellurium thin films can be successfully used for the detection of toxic gases and environment monitoring [1-3].

Firstly, the microcrystalline Te films grown on the glass Pyrex substrates were shown to be sensitive to nitrogen dioxide in ambient air [4,5]. Soon, it was found out that some other gases as CO, $H_2S$, or propyllamine [6,7] can be successfully detected at room temperature, but the sensitive parameters can be affected by technological conditions of the sensor preparation [8]. In the last communication it was observed that the increasing of the substrate temperature, results in increase the tellurium grain dimensionality. The microstructures of the substrate influence the gas sensitivity, as well. So, the films deposited on the glass substrate show the maximum sensitivity to $H_2S$ and $NO_2$, while those deposited on sapphire substrate show a minimal sensitivity [8].

In the present work the tellurium films have been prepared by different rates of growing on different substrates, not heated and not cooled, which allowed to establish the influence of both deposition rate and substrate microstructure on gas sensitivity.

## 2. MATERIALS AND METHODS

Tellurium (purity 99.999 %) based thin films of different thicknesses were deposited either onto Pyrex glass or nanostructured $Al_2O_3$ substrates with thermal vacuum evaporation. The evaporation was performed from a tantalum boat at the working pressure of $\approx 10^{-4}$ Pa, without heating or cooling the substrate. The growing rate of the film was varied from 1,0 to 30 nm/s, the area of deposition being around 70 $mm^2$. Rectangular samples of different thicknesses were prepared by variation of evaporation time, while the distance between the evaporation boat and the substrate has been kept the same - 20 cm. The thicknesses and the shape of the films have been measured after their preparation using an Atomic Force Microscope (AFM) (SIS SCAN Control/C). The surface morphology of the films was investigated, using a VEGA TESCAN TS 5130 MM scanning electron microscope (SEM). X– ray analyses using the DRON –YM1 diffractometer by Fe$K\alpha$ radiation was applied for the structural investigations of the grown films. Rotation velocity of the scintillation counter was 2 (or / and 4) angle degrees /min.

Two Indium pillows were pressed on top of the Te film surface in order to serve as electrical contacts for the gas-sensing element. The distance

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between electrodes was ~ 5mm so that the sensing aria consists of about 30 mm$^2$.

$NO_2$ vapor with a concentration of 0.15 to 1.0 ppm was obtained by using the experimental set up described in [9]. The thin film sensing devices were put into a test cell (of 10 ml volume) and the gases were injected with a flow rate of 100 ml /min, maintained by mass flow controllers (MFC, Wigha, Germany), parallel to the film surface.

Humidification of the carrier gas was accomplished using saturated solution of the salt $CaCl_2$ in water with relative humidity of 32%, and the platinum resistance temperature detector PT – 100 close to the sensor served as a temperature controller. The current transient characteristics have been carried out with different gas concentrations at room temperature with an applied voltage of 5V. In order to transform the resistance signal into voltage signal, the sample was connected in series to a load resistance using a direct current (d.c) voltage supplier. In all measurements, the load resistance was chosen to be approximately by an order of magnitude less than the sample resistance.

The sensor sensitivity was defined as a relative variation of the resistance expressed in percent / ppm:

$$S = \frac{R_a - R_g}{cR_a}\mathbf{x100} \qquad (1)$$

were $R_a$ and $R_g$ are the electrical resistance of the sensor in air and in the presence of gas ($NO_2$) respectively, and $c$ is concentration of the target gas [ppm].

## 3. RESULTS AND DISCUSSIONS

### *3.1. SEM and X-Ray analyses*

To clarity the effect of deposition rate on microstructure, tellurium thin films were grown on Pyrex substrates and both X-Ray and SEM analyses have been used.

Figure 1 shows the SEM images of as-prepared Te thin films grown with deposition rate v = 1nm/s. It is seen that the film deposited with so low rate, exhibits a dense layer of polycrystalline Te with a crystallites size of about 0.5 to 1.0 μm, oriented along the substrate. The X-Ray diffraction pattern of such films (Figure 2) indicates the hexagonal phase of Tellurium crystallites.

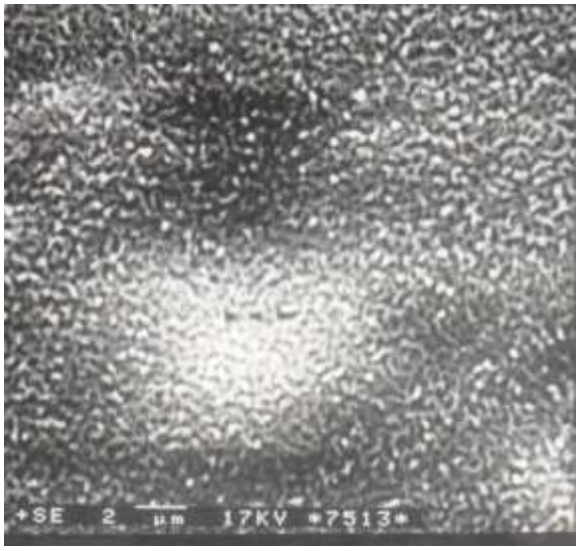


*Figure 1. SEM micrographs of Te grown on Pyrex with on deposition rate v = 1nm/s*

*Slika 1. SEM mikrografije Te na Pyrex staklu sa brzinom taloženja v = 1nm/s*

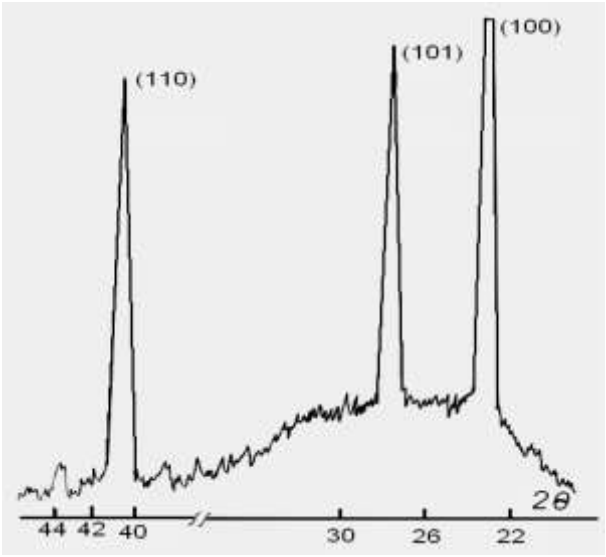


*Figure 2. XRD diffraction micrographs of Te grown on Pyrex with deposition rate v = 1 nm/s*

*Slika 2. XRD difrakcione mikrografije Te na Pyrex staklu sa brzinom taloženja v = 1 nm/s*

Increasing of the film deposition rate up *to v = 10 nm/s* results in transition from microcrystalline structure of the films to a nanocrystalline one (Figure 3)". Figure 4 shows a typical XRD pattern of a nanocrystalline tellurium film grown with a deposition rate v=10nm/s. This figure also confirms both the nanometric dimensionality of crystallites and the absence of preferential grow orientation.

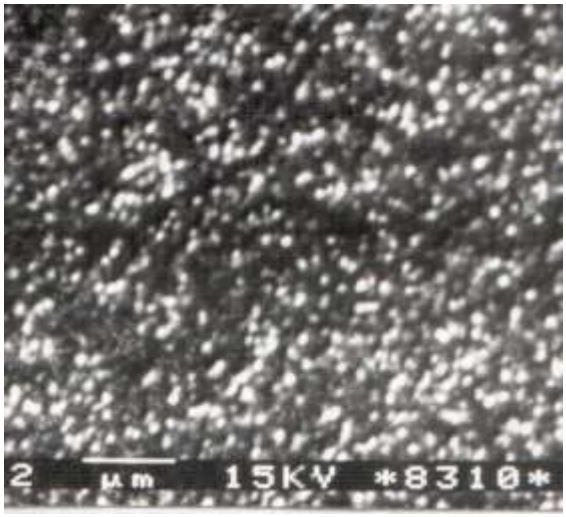


*Figure 3. SEM micrographs of Te grown on Pyrex with on deposition rate v = 10 nm/s*

*Slika 3. SEM mikrografije Te na Pyrex staklu sa brzinom taloženja v = 10 nm/s*

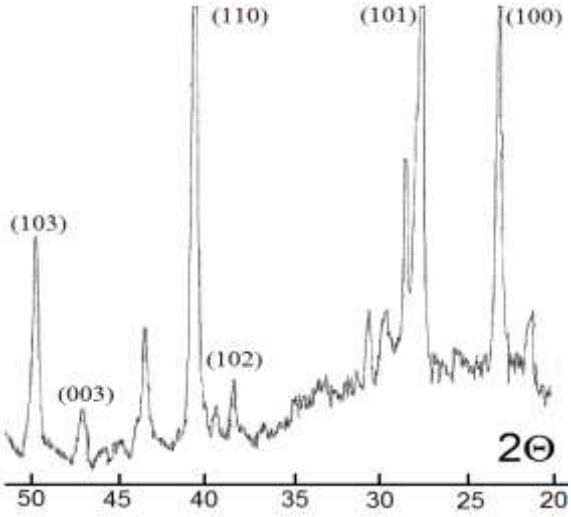


*Figure 4. XRD diffraction micrographs of Te grown on Pyrex with deposition rate v = 10 nm/s*

*Slika 4. XRD difrakcione mikrografije Te na Pyrex staklu sa brzinom taloženja v = 10 nm/s*

Figure 5 shows the SEM micrographs of Te fine film deposited on Pyrex substrate with a deposition rate of.*v = 30 nm/s*. From this figure we can observe that the surfaces of these films are smooth and without any traces of crystallites.

Figure 6 shows the XRD diffraction pattern of amorphous Te-films of thicknesses 110 nm. Dotted lines show the places corresponding to peaks of crystalline Te with orientation indicated by round brackets. The peaks corresponding to Te were not found, indicating the predominantly amorphous nature of film.

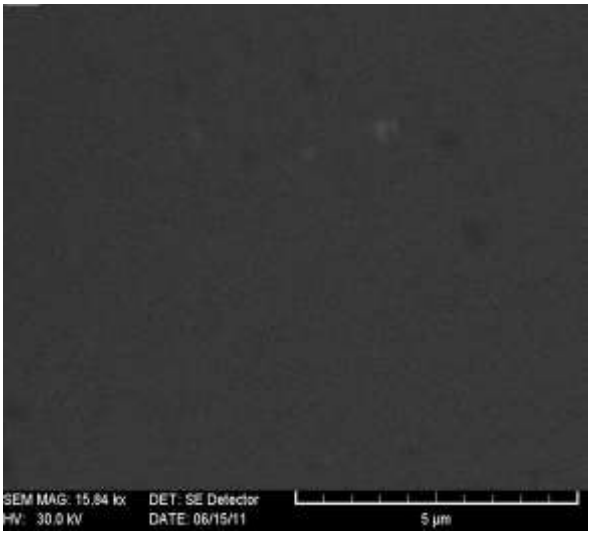


*Figure 5. SEM micrographs of Te grown on Pyrex with on deposition rate v = 30 nm/s*

*Slika 5. SEM mikrografije Te na Pyrex staklu sa brzinom taloženja v = 30 nm/s*

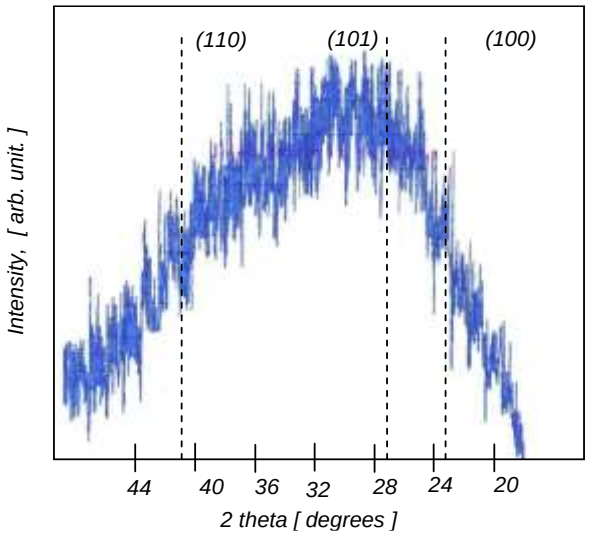


*Figure 6. XRD diffraction micrographs of Te grown on Pyrex with deposition rate v = 30 nm/s*

*Slika 6. XRD difrakcione mikrografije Te na Pyrex staklu sa brzinom taloženja v = 30 nm/s*

The substrate's influence on film morphology and structure has been studied through the preparation and structural analysis of Te films grown onto the both Pyrex glass and sintered ceramic $Al_2O_3$ substrates, using the deposition rate of 30 nm/s.

Figure 7 shows the SEM images of tellurium films grown on sintered alumina ($Al_2O_3$). In contrast with similar films grown on glassy Pyrex substrates (Figure 5) these films consist of interconnected islands. At the same time, on the XRD diffraction

pattern of Te deposited on the $Al_2O_3$ substrate (Figure 8) a highlighted peak of Alumina, appears along and the presence of two pronounced Te peaks.

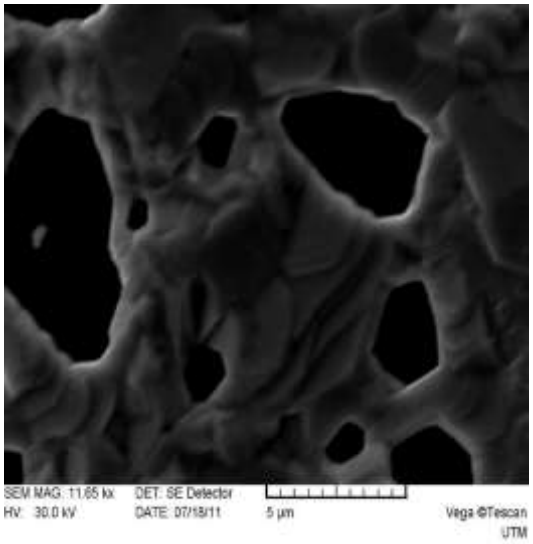


*Figure 7. SEM micrographs of Te film deposited on $Al_2O_3$ substrate with deposition rate v = 30 nm/s*

*Slika 7. SEM mikrografije Te filma deponovanog na $Al_2O_3$ podlogu sa brzinom taloženja v = 30 nm/s*

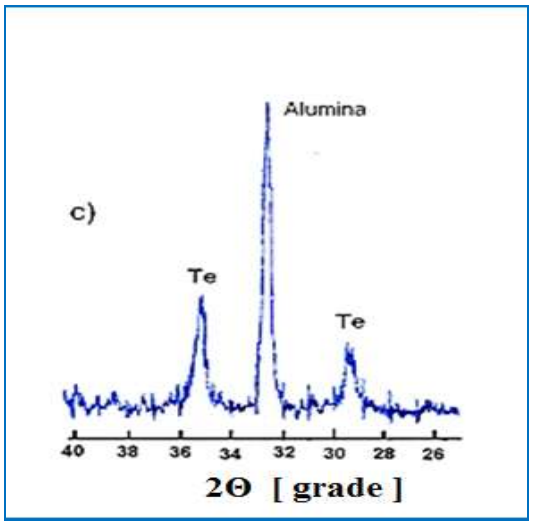


*Figure 8. XRD diffraction micrographs of Te get o $Al_2O_3$ substrate with deposition rate v = 30 nm/s*

*Slika 8. XRD difrakcione mikrografije Te filma deponovanog na $Al_2O_3$ podlogu sa brzinom taloženja v = 30 nm/s*

### *3.2 Gas sensing characterization*

Figures 9 show the dynamic response of tellurium films deposited on the Pyrex substrate with different rates.

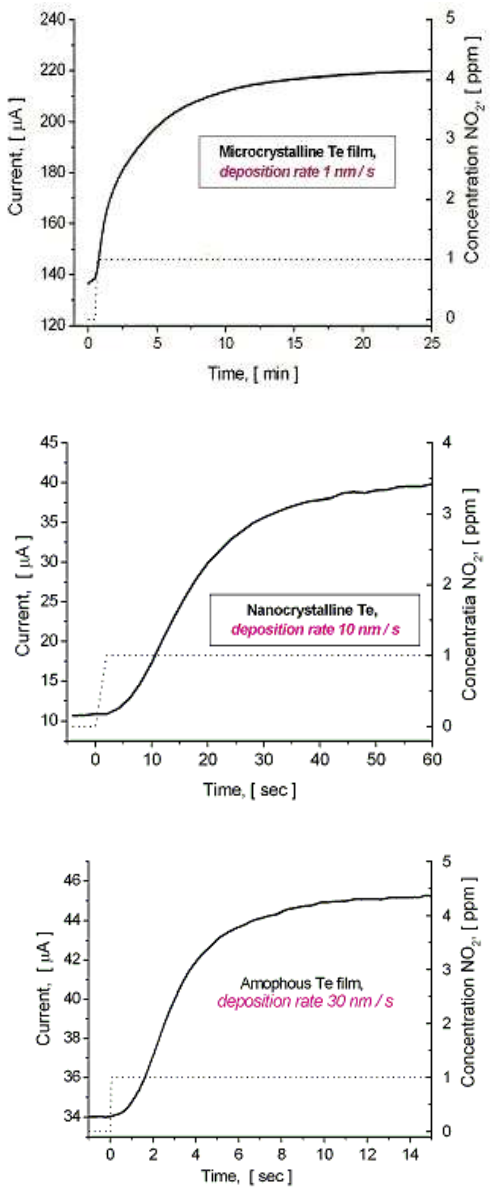


*Figure 9. Dynamic response at room temperature of Te thin films grown by different rates on glass substrates*

*Slika 9. Dinamički odziv na sobnoj temperaturi Te tankih filmova dobijenih pri različitim brzinama na staklenim podlogama*

It can be observed that the modification of film's structure from microcrystalline to nano-crystalline and further to amorphous one leads to a noticeable diminishing of the response time.

Diagrams shown on figures 10 and 11 illustrate both the dependence of the response time and sensitivity to $NO_2$ of tellurium films on their grown rate. It is seen that amorphous thin films exhibit the shortest response time of about 10s, which is 60 times less than response time for microcrystalline films. On the other hand, these diagrams indicate

that the sensitivity to nitrogen dioxide monotonically decreases from 40% for microcrystalline films to about 30 % for nanocrystalline and further to only 20 percent for amorphous films. Thus, the microcrystalline – nanocrystalline – amorphous transition results in a slight decreasing of gas sensitivity (~ 20 %) accompanied by sharp fall (~ 60 times) of response time, which agrees with results reported in [10].

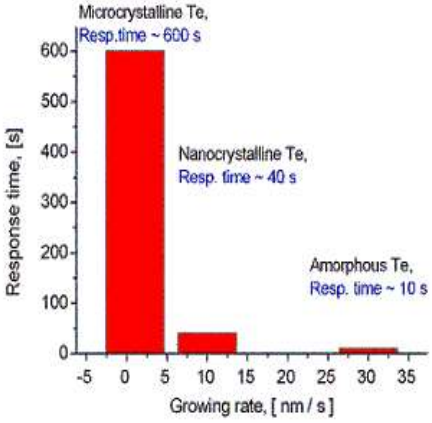


*Figure. 10. The response time of Te thin films grown by different rates*

*Slika 10. Vreme odziva Te tankih filmova dobijenih pri različitim brzinama*

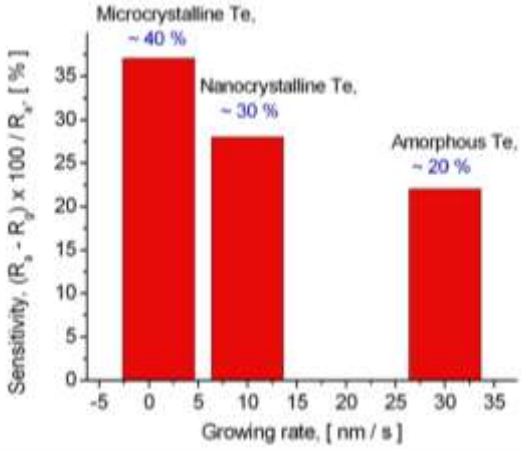


*Figure 11. The sensitivity of Te thin films to 1 ppm of $NO_2$*

*Slika 11. Osetljivost Te tankih filmova na 1 ppm $NO_2$*

Figures 12 and 13 show the current flow through tellurium thin (~ 110 nm) films grown on Pyrex-glass and nanostructured $Al_2O_3$ substrates respectively, under repeated switching on-off of the $NO_2$ gas mixture at constant bias voltage, room temperature (25 $^0$C). The dotted line gives the switching schedule.

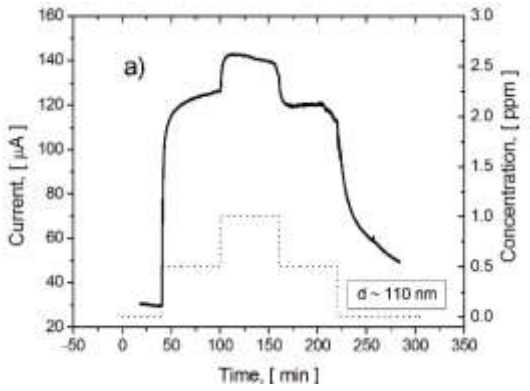


*Figure 12. Transient characteristics of gas - induced current by exposure of Te films (thickness ~110 nm) to various concentrations of $NO_2$ according to the profile shown in dotted lines of the bottom. Substrate: Pyrex –glass*

*Slika 12. Prelazne karakteristike gasa izazvane indukovanom strujom izlaganjem Te filmova (debljina ~ 110 nm) različitim koncentracijama $NO_2$ prema profilu prikazanom isprekidanim linijama dna. Podloga: Pyrex - staklo*

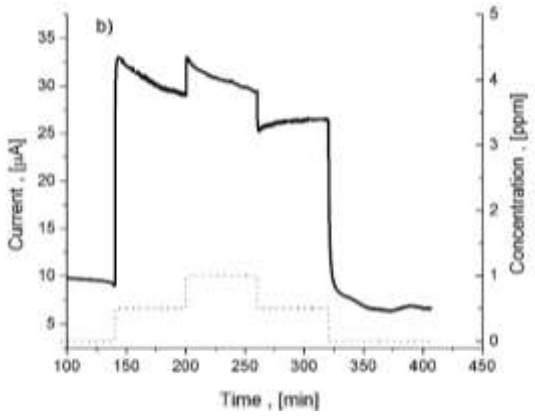


*Figure 13. Transient characteristics of gas - induced current by exposure of Te films (thickness ~110 nm) to various concentrations of $NO_2$ according to the profile shown in dotted lines of the bottom. Substrate: Nanostructured $Al_2O_3$*

*Slika 13. Prelazne karakteristike gasa izazvane indukovanom strujom izlaganjem Te filmova (debljina ~ 110 nm) različitim koncentracijama NO2 prema profilu prikazanom isprekidanim linijama dna. Podloga: Nanostrukturirani $Al_2O_3$*

It is seen that the current follows the schedule showing a usual behavior: the transition of concentration from 0.5 to 1.0 ppm of $NO_2$ results in increasing of current [11]. The recovery time is longer than response time, which consists only a few seconds. There is no also a noticeable baseline drift.

It is clearly seen, that the substrate microstructure, i.e. the growing of the film on nanostructured

dielectric ($Al_2O_3$) instead of growing on a continuous Pyrex – glass substrate results in an evident shortening of response times. The films grown on nanostructured $Al_2O_3$ show a considerably short response time. The gas concentration increases results in extinction of sensitivity of the film.

## 4. CONCLUSIONS

The phase-structure and gas sensitivity peculiarities of Te films strongly depend on both substrate microstructure and growth rate. The increasing of deposition rate results in transformation of microcrystalline structure to a nanocrystalline one and further to amorphous state of the film, accompanied by a slight diminishing of sensitivity to $NO_2$ at room temperature. Simultaneously the response time, decreases by 2 orders of magnitude, constituting only a few seconds.

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## 5. REFERENCES

[1] D.Tsiulyanu (2006) Chalcogenide Semiconductor Based Gas Sensors, In: C.A. Grims, ed., Encyclopedia of Sensors, American Scientific Publishers, USA, 2, 113-124.

[2] S.Sen, S.Gupta, V.Sahni (2007) Telurrium Thin Films Based Gas Sensor. In: Aswal, D., Gupta, S., Science and Technology of Chemiresistor Gas Sensors., Nova Science Publishers Inc., New York, 257–296.

[3] D.Tsiulyanu (2011) In: Reithmaier J., Tellurium Thin Films in Sensor Technology, Nanotechnological Basis for Advanced Sensors, Springer, Berlin, 363–380.

[4] D.Tsiulyanu, S.Marian, V.Miron, H-D.Liess (2001) High sensitive tellurium based $NO_2$ gas sensor, Sensors and actuators B, 73, 35-39.

[5] T.Siciliano, M.Di Giulio, M.Tepore, E.Filippo, G.Micocci, A.Tepore (2008) Tellurium sputtered thin films as $NO_2$ gas sensors, Sensors and Actuators B, 135, 250–254.

[6] D.Tsiulyanu, S.Marian, H-D.Liess (2002) Sensing properties of tellurium based thin films to propylamine and carbon oxide, Sensors and Actuators B, 85, 232-238,

[7] S.Sen, V.Bhandarkar, K.Muthe, M.Roy, S. Deshpande, R.Aiyer, S.Gupta, J.Yakmi, V.Sahni (2006) Highly sensitive hydrogen sulphide sensors operable at room temperature, Sensors and Actuators B, 115, 270-275.

[8] V.Bhandarkar, S.Sen, K.Muthe, M.Kaur, M.Kumar, S.Deshpande, S.Gupta, J.Yakmiand, V.Sahni (2006) Effect of deposition conditions on the microstructure and gas-sensing characteristics of Te thin films, Materials Science and Engineering, 131, 156–161.

[9] R.Cabala, V.Meister, K.Potje–Kamloth (1997) Effect of competitive doping on sensing properties of Polypyrrole, Journal of the Chemical Society, Faraday Transactions articles, 93, 131-137.

[10] D.Tsiulyanu, A.Moraru (2014) Nanocrystalline Tellurium films: Fabrication and gas sensing properties, Nanoscience Advances in CBRN Agents Detection, Information and Energy Security, Springer, Sozopol, 389-409.

[11] D.Tsiulyanu, O.Mocreac (2013) Concentration induced damping of gas sensitivity in ultrathin tellurium films, Sensors and Actuators B, 177, 1128-1133.

## IZVOD

## UTICAJ BRZINE DEPOZICIJE I MIKROSTRUKTURE SUBSTRATA NA GASNU OSETLJIVOST Te - TANKIH FILMOVA

*Telur tanke folije pripremljene su korišćenjem različitih brzina (0,1 ÷ 30 nm/s) fizičkim taloženjem u vakuumu na staklu, sinterovanoj glinici i elektrohemijski nanostrukturnim $Al_2O_3$ supstratima. Osetljivost proizvedenih filmova na gas azot-dioksid testirana je na sobnoj temperaturi. Pokazano je da brzina taloženja snažno utiče na mikrostrukturu filmova o kojima je reč, kao i na njihova senzorna svojstva prema gasu. Povećanje brzine taloženja rezultira transformacijom mikrokristalne strukture filma u amorfnu. Istovremeno se smanjuje i osetljivost na gas i vreme odziva. Rezultati su objasnjeni u smislu interakcije između molekula gasa i usamljenih elektrona atoma telura.*

***Ključne reči:*** *brzina taloženja, osetljivost na gas, vreme odziva, supstrat, tanki film.*

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