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CHARGE TRANSPORT AND GAZ SENSING PECULIARITIES OF NANOCRYSTALLINE AND AMORPHOUS TELLURIUM FILMS

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Abstract. Nanocrystalline and amorphous tellurium thin films have been prepared and their both DC and AC electrical conductivity was investigated to receive the information concerning mechanisms of charge transport at different temperatures, environments and frequencies of the applied electrical field. SEM and XRD analysis have been used for structural investigation of the films but the impedance spectroscopy was applied for the transport mechanisms determination. Effect of the environment was studied by application of small concentrations of nitrogen dioxide, paying attention to both times and magnitude of response, followed by recovery of origin state after the target gas is removed. It is shown that the nanocrystalline structure of the film can be transformed into an amorphous one through growth rate increase. Such transformation however, does not affect the mechanism of charge transport up to frequencies of 10^5 Hz, which is due to electrical charge carriers excited above mobility band gap edges. At higher frequencies, the AC conductivity of amorphous films strongly increases with frequency increase, which is explained by transition to another transport mechanism that includes the charge carriers hopping via localized states in the gap. Both nanocrystalline and amorphous films react with nitrogen dioxide diluted in an air environment but their gas - sensing parameters differ. Results are explained in terms of interaction between gas molecules and lone – pair electrons of tellurium atoms influenced by roughness (compactness) of the films disturbed at disordering (amorphisation) increase.

Keywords: *Telurrium films, charge transport, adsorption, NO_2.*

1. Introduction

Tellurium based films may be used for harmful gases detection at room temperature [1, 2] that allows miniaturization of sensitive gas devices. Firstly, in the early 2000s the microcrystalline Te thin films were shown to exhibit high sensitivity to low (ppm range) concentrations of nitrogen dioxide [3]. Later, there were also found out the remarkable

sensitive properties of microcrystalline Te films toward ammonia [4, 5], hydrogen sulfide [6], carbon dioxide and amines [7]. Over the past years, due to general increasing interests to nanodimensional bodies and structures, a great attention is given to growing, study and application of nanostructured and amorphous tellurium for gas sensing. Different, sometimes quite sophisticated methods to obtain nanostructured tellurium have been proposed. Firstly, the works were conducted to grow the nanocrystalline Te films via either thermal vacuum evaporation [8, 9] or sputtering (13.6 MHz) in ultra-high-purity argon [10] of pure
Te onto the Pyrex glass, alumina, oxidized silicon or sapphire substrates. These films have been tested to detect both oxidizing (NO_2) and reducing (H_2S) toxic gases at temperatures between 77 and 423 K. Further the investigations have been extended to Te nanotubes grown onto quartz or Si (111) substrates by a catalyst-free growing process in a furnace filled with argon [11], as well as by their growing onto silicon substrates containing the preliminary deposited nanoparticles of silver or gold as template, using the high vacuum deposition technique [12]. In both cases the Te nanotubes of about 50 nm in diameter have been grown, which have shown remarkable sensitivities toward different toxic gases, including NO_2. An increasing of gas sensing performance was achieved also via growing either the single - crystal Te nanotubes / nanowires via hydrothermal recrystallization [13] or amorphous Te films onto not cooled heated Pyrex substrates [14]. For further advancement in nanostructured and amorphous tellurium application, including the field of gas sensitive devices, the theoretical and experimental works are required conducted to elucidate the fundamental physical parameters of tellurium in both these states as well as at transition from nanostructured state to amorphous one. In this respect, the present paper is devoted to growing both nanocrystalline and amorphous thin tellurium films, study their electrical conductivity of direct and alternating current at different temperatures and frequencies of applied voltage conducted to elucidate the band gap parameters and mechanisms of charge transport. Alongside, the gas (NO_2) sensing properties of these films have been studied in a wide frequency range at room temperature.

2. Experimental procedures

Tellurium (purity 99.999 %) based thin films have been prepared by thermal vacuum evaporation onto Pyrex glass substrates. The evaporation has been performed from tantalum boats onto unheated and not cooled substrates, at working pressure ~ 10^{-4} Pa. The films were prepared using both 10 nm/s and 30 nm/s, which has been achieved via temperature variation of evaporator, while keeping constant its distance till substrate. The surface morphology and the phase state structure were investigated using a VEGA TESCAN TS 5130 MM scanning electron microscope and the DRON –YM1 diffractometer by FeK radiation respectively. In the last case, the rotation velocity of the scintillation counter was 2 (or / and 4) angle degrees /min. The electrical characterization was conducted to find out the fundamental parameters of the material that control the transport mechanisms, such as the mobility gap and the minimum metallic conductivity. For this purpose the films were supplied either with symmetric ohmic platinum contacts grown via cathode scattering or from silver ones, painted using the Ag paste of the "Kontactol" type. The DC measurements were carried out in a temperature range of 10 -180^{0}C. The AC measurements were performed in a frequency range of 10^3-10^6 *Hz,* using a HP 4192A impedance analyzer. The thin film device was fixed onto an electrical refrigerator, allowing cooling the sample until

10^0C, but both these two pieces that is the film and refrigerator, were then placed into a stove for subsequent heating. A platinum resistance temperature detector PT – 100 close to the film has been used to assist temperature control. Data processing was performed with PC and a data acquisition board manufactured by National Instruments Inc. In all cases applied voltage varied between –5V and +5V with a step of 20 mV and the respective values of the current were measured. Delay time between measurements was 2 seconds.

The gas sensing characterization of Te based functional structures was performed using NO_2 vapor of different concentrations obtained from calibrated permeation tubes (Vici Metronics, USA) incorporated into the experimental set-up described in our previous paper [15]. Thin film devices were put into a test cell (of 10 ml volume) in which the gases were injected parallel to the film surface. Mass flow controllers (MFC, Wigha, Germany) maintained constant flow (100 ml/min). The measurements were carried out at different temperatures in either dry air or its mixture with NO_2 vapor.

3. Results and Discussions

3.1 SEM and X-ray diffraction analyses

Figure 1a shows SEM image of a tellurium film grown with a deposition rate $v = 10nm/s$ onto the glass Pyrex substrate. It can be observed the nanometric dimensionality of crystallites as well as absence of some preferential orientation of their grow.

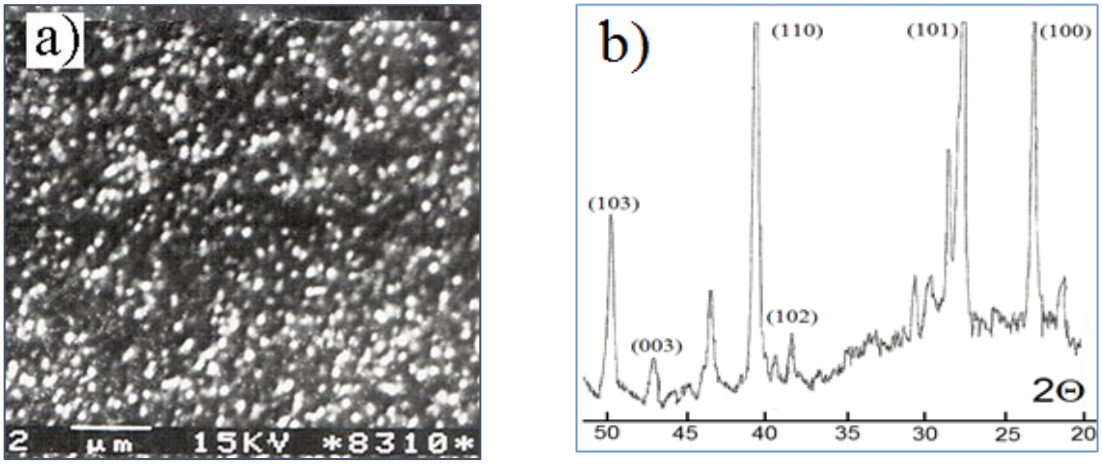

Figure 1. a) SEM micrographs and b) XRD diffraction pattern of a Te thin film grown onto Pyrex glass substrate with a deposition rate of $v = 10nm/s$.

The XRD diffraction pattern of such a film is depicted in Figure 1b. It is seen that XRD pattern shows the films to be highly crystalline and having a predominant hexagonal phase of Te. The positions of highest peaks matched the standard values: the first peak is due to reflection from the (100) crystal plan, the second peak is observed due to reflection from the (101) crystal plan but the third peak – due to reflection from (110) crystal plan.
The nearly equal intensities of these peaks, as well as the appearing of other diffraction peaks, confirms the absence of a predominant growth orientation of the nanocrystals. Figures 2(a) and 2(b) show the SEM micrograph and XRD diffraction pattern of tellurium thin films deposited onto Pyrex substrate with a deposition rate of 30 nm/s respectively. It is seen that the surfaces of these films are smooth and without any traces of crystallites. XRD diffraction patterns do not comprise any peaks corresponding to crystalline tellurium that indicates the predominantly amorphous state of such films.

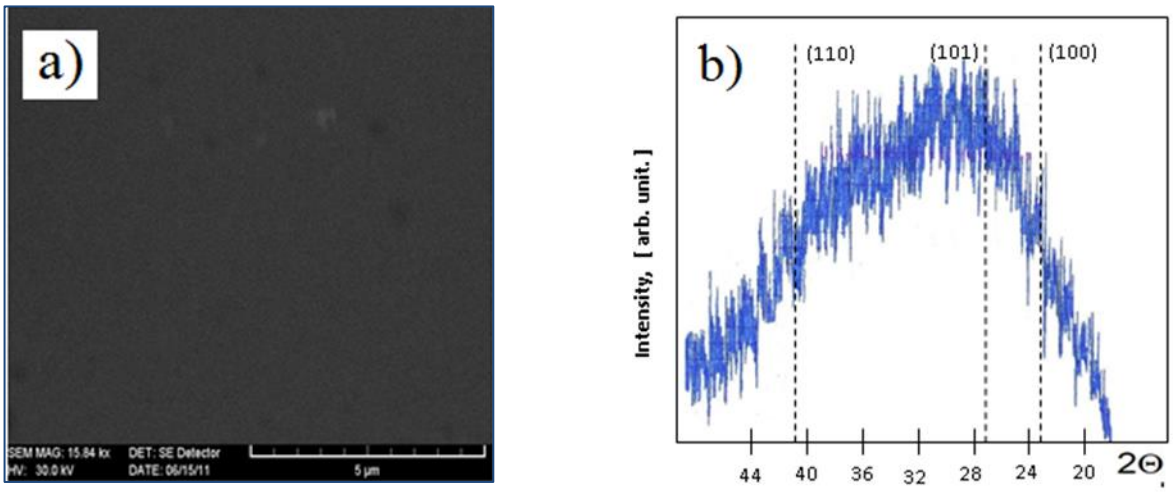

Figure 2. a) SEM micrographs and b) XRD diffraction pattern of Te films grown on Pyrex glass substrates with a deposition rate $v = 30nm / s$

3.2 DC and AC conductivity

Figure 3 shows the plot of DC conductivity versus reciprocal temperature for both nanocrystalline and amorphous tellurium films in an usual air atmosphere. It is seen that along the entire range of applied temperature the conductivity of nanocrystalline films is by approximately three orders of magnitude higher than of amorphous ones.

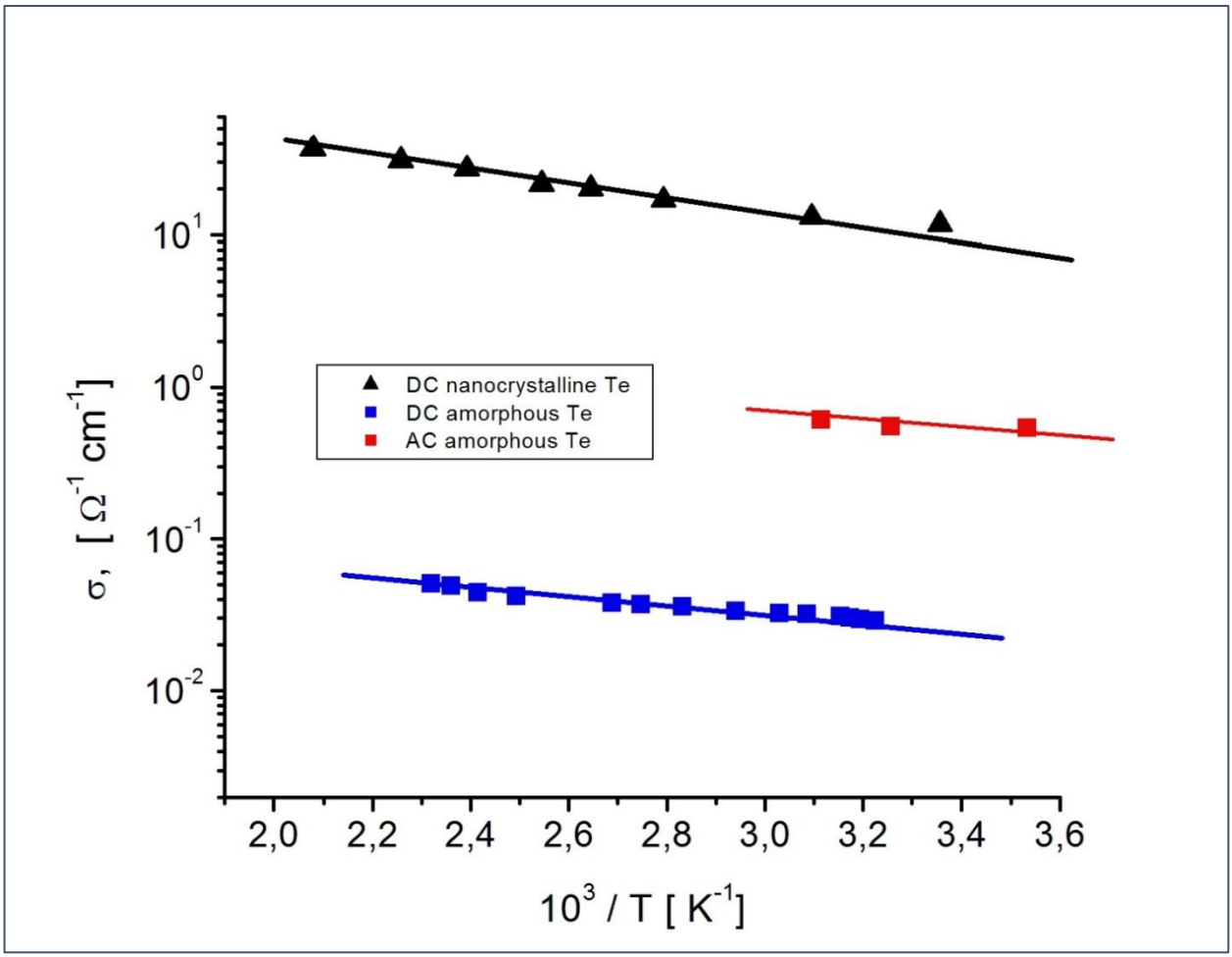

Figure 3. DC and AC conductivity of nanocrystalline and amorphous tellurium films versus reciprocal temperature.

On the other hand, for both nanocrystalline and amorphous tellurium films, the dependence $ln\sigma$ - $10^3/T$ shows the similar direct lines with approximately the same slope. Therefore, both kind of films under investigation can be atributed to high disordered semiconductors, but the linear dependences $ln\sigma$ - $10^3/T$ indicate to a single charge transport mechanism, realized via extended states above mobility edges. The theoretical model developed by Mott and Davis [16], for such semiconductors describe their electrical conductivity via expression:

$$\sigma_{ext} = C \exp\left(-\frac{E_F - E_V}{kT}\right) \quad (1)$$

where E_V and E_F is the mobility edge of the valence band and Fermi level respectively, k is the Boltzmann constant and T the absolute temperature. Assuming that the gap $E_1 = E_F - E_V$ decreases linearly with the temperature increase, that is $E_F - E_V = E_0 - \gamma T$, equation 1 looks as:

$$\sigma_{ext} = \sigma_{\min} \exp\left(-\frac{\gamma}{T}\right) \exp\left(-\frac{E_0}{kT}\right) \quad (2)$$

where σ_{min} is the minimum metallic conductivity, that is the conductivity at the energetic level corresponding to valence band mobility threshold, γ is the temperature coefficient of the optical gap, E_0 - is the value of the energy between the Fermi level and the edge of the valence band extrapolated to the temperature $T = 0$. Taking $\gamma = 2 \cdot 10^{-4} eV / degree$ [16], the experimental values of E_0 and C have been estimated (Table 1).

Table 1

Semiconducting parameters of tellurium films

Charge transport mechanism		C ($\Omega^{-1} cm^{-1}$)	E_1 (eV)	E_g (eV)	σ_{min} ($\Omega^{-1} cm^{-1}$)
Extended band states	amorphous tellurium	0,22	0,17	≈ 0,34	0.022
	nanostructured tellurium	387,4	0,172	≈ 0,34	38,74

These results are compatible with the ones obtained for amorphous tellurium films grown via low rates of deposition onto high cooled (125K) substrates [17], as well as with following investigations provided on AC.

Figure 4a shows the spectral dependence of AC conductivity of amorphous tellurium films at several temperatures.

It is seen that the dynamic conductivity of such films increases with temperature increase, but practically do not depend on the frequency up to approximatelly 10^5 Hz.

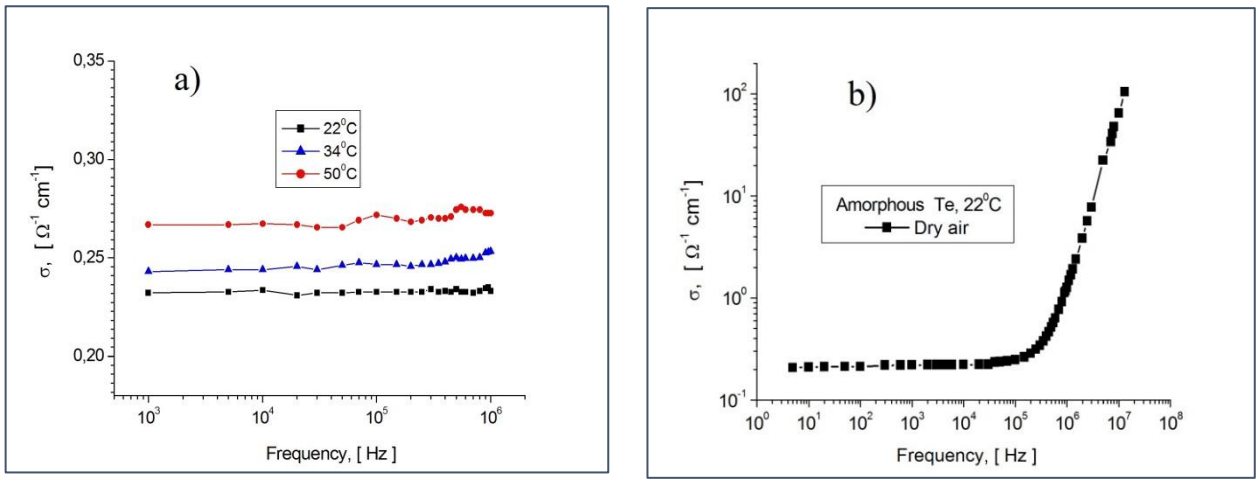

Figure 4. The spectra of AC conductivity of nanocrystalline (a) and amorphous (b) tellurium films.

Such behavior means that in the frequency range up to10^5Hz the transport mechanism is due to electrical charge carriers excited above mobility band gap edges that is via extended states.

The spectral distribution of AC conductivity of an amorphous Te film at room temperature (22^0C) is depicted on Figure 4b. Comparison of AC spectra of nanostructured and amorphous Te films indicates their compatibility at frequencies less than 10^5Hz. In this frequency range, the AC conductivity of amorphous thin films does not depend on frequency but, as shown in Figure 3, it also increases with temperature increase. At higher frequencies, the AC conductivity of amorphous tellurium films (Figure 4b) becomes strongly frequency dependent, which is due to arising of additional transport mechanisms, including the mechanism caused by carriers hopping via localized states in the gap [16].

3.3 Effect of NO_2 adsorption

Figure 5 shows the DC currents flow through both nanocrystalline and amorphous thin tellurium films grown on Pyrex substrate, under repeated switching on-off of the NO_2 gas mixture, at constant bias voltage and room temperature (22 ^{0}C).

The dotted line at the bottom gives the switching schedule. It is seen that both films react with target nitrogen dioxide, following the schedule of its concentration in the applied gaseous mixture. Although the transient characteristics of these kinds of films look quite similar, the transition from a nanocrystalline structure to an amorphous one slightly affects both their electrical conductivity and gas - sensing parameters.

The diagram inserted in Figure 5 shows a comparison of sensitivities of the films in question, estimated as relative decreasing of the electrical resistance in %, by application of 1,0 ppm of NO_2 at room temperature. This diagram indicates that the transition from nanocrystalline to amorphous state diminishes the sensitivity to nitrogen dioxide of tellurium based films by approxomately 10 percent. Certainly, as it is shown in our previous works, as well as in the works of other authors [2, 8], the sensitivity of tellurium films depends also on temperature, post preparing annealing, thickness of the film etc. The DC current increase by nitrogen dioxide adsorption is explained by chemisorption of the NO_2 molecules, their interaction with the pair of electrons of chalcogen atoms, which results in releasing additional majority carriers (holes) by the surface [10, 14].

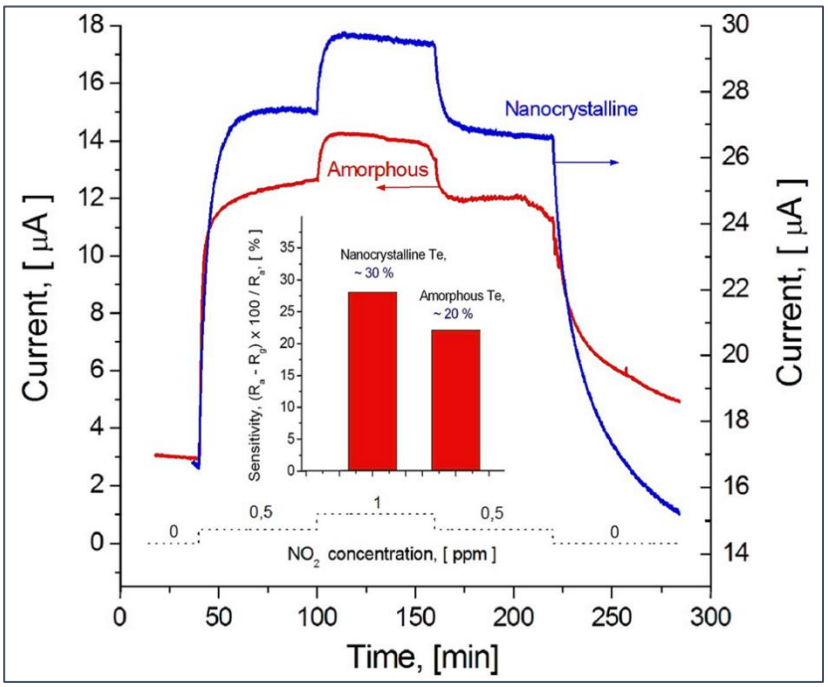

Figure 5. Transient characteristics of gas - induced current by exposure of tellurium thin films to various concentrations of NO_2 at room temperature. Inserted diagram shows a comparison of sensitivity to 1 ppm NO_2 of a nanocrystalline film with an amorphous one.

As the dynamic conductivity of amorphous tellurium films strongly depends on frequency of applied electric field (Figure 4b), it seems interesting to elucidate the effect of target gas (NO_2) on AC conductivity spectra. Figure 6 shows the effect of nitrogen dioxide on dynamic conductivity spectra of amorphous Te films at room temperature.

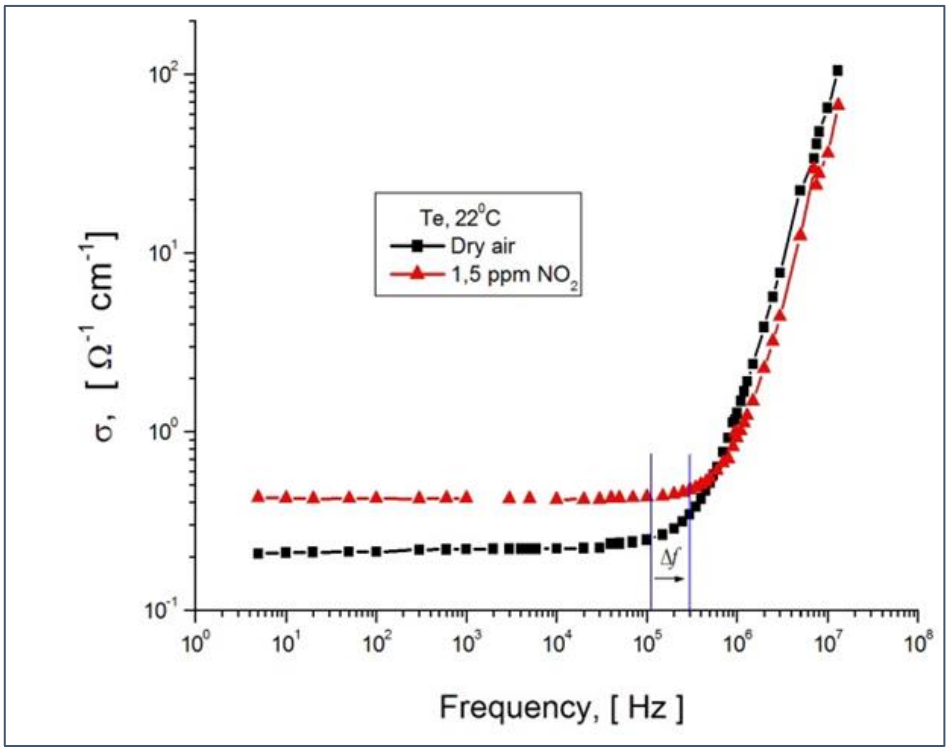

Figure 6. The conductivity spectra of amorphous Te films in different gaseous environments, at room temperature.

It can be observed that addition of nitrogen dioxide to dry air leads to both the increase of AC by approximately one order of magnitude and prolongation of its independence of frequency in a narrow frequency range around 10^5 Hz.

Such prolongation has been early observed also in quaternary glassy $As_2Te_{13}Ge_8S_3$ films [18] although in a more extended frequency range. The explanation was provided in terms of modification of the dominant mechanism of charge transport at the surface by gas absorption.

In common conditions, without application of nitrogen dioxide, the conductivity $\sigma(\omega)$ in surroundings of 10^5 Hz is due to charge carriers hopping via localized states of the band tails. The application and absorption of NO_2 molecules result in a sharp increase of free holes concentration at the surface due to interaction of dangling bonds with lone pairs of chalcogen atoms. So, the conditions are created to provide the conductivity via extended states till frequencies $\omega > 10^5 Hz$, the transport mechanism due to hopping via localized states in the vicinity of Fermi level, pinned near center of the forbidden gap, becomes predominant.

4. Conclusions

The phase-structure and gas sensitivity peculiarities of Te films strongly depend on their grown rate. The film deposition rate increase results in transformation of nanocrystalline structure of the film into an amorphous or predominant amorphous one. Such transformation however does not affect the mechanism of charge transport up to frequencies of 10^5 Hz, which is due to electrical charge carriers excited above mobility band gap edges. The width of the mobility gap has been assessed as $E_g \approx 0,34eV$ for both nanocristalline and amorphous tellurium films. At the same time, the minimum metallic conductivity essentially differs for these kinds of films as $\sigma_{\min} \approx 0,022\Omega^{-1}cm^{-1}$ for the amorphous tellurium film and $\sigma_{\min} \approx 34,74\Omega^{-1}cm^{-1}$ for a nanocrystalline one.

At higher frequencies than 10^5Hz, the AC conductivity of amorphous films strongly increases with frequency increase, which is explained by transition to another transport mechanism that includes the charge carriers hopping via localized states in the gap. Both the nanocrystalline and amorphous films react with nitrogen dioxide diluted in an air environment, but the gas - sensing parameters, including sensitivity; differ due to effect of disordering increase, caused by amorphisation.

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