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In-depth evolution of tellurium films deposited by Frequency Assisted Thermal Evaporation in Vacuum (FATEV)

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Abstract. In order to enlighten the in-depth organization of thin tellurium films, deposited by the frequency assisted thermal evaporation in vacuum (FATEV) approach, morphological, structural and spectroscopic investigations were performed. Spectroscopic ellipsometry (SE) and cross-section scanning electron microscopy (SEM) showed a change of the growth mechanism upon application of higher vibrations’ input frequencies during the films deposition. The films, deposited by conventional thermal evaporation in vacuum with no vibrations applied, as well as these, deposited by FATEV with application of 50 Hz vibrations, were characterized by initial densification followed by 2D nanoparticles growth when a certain threshold thickness was reached. On the other hand, the high-frequency vibrations of 4 and 10 kHz preconditioned growth of tellurium nanoribbons oriented towards the z-axis from the very beginning of the film formation. The topography changes, observed by atomic force microscopy (AFM) and scanning electron microscopy, showed highly porous surfaces (with high root mean square surface roughness) formed by distinct nanoblades for the films, deposited at low input frequencies, while the films, deposited under the impact of vibrations in the kilohertz range, were much more ordered, and hence their surface was significantly smoother. The structural parameters of the samples were investigated by X-ray diffraction (XRD) analysis.

1. Introduction
The frequency assisted thermal evaporation in vacuum (FATEV) is a new approach for physical vapor deposition (PVD) of thin films. It is based on application of mechanical vibrations with audio frequencies on the substrate during condensation of an evaporated material. The technological specifics and the range of FATEV application, determined until now, are widely described in our previous works [1, 2]. As the method is still under evaluation only the changes of the deposits’ surface have been studied. It has been found that the application of vibrations with frequencies from the lower part of the audio spectrum leads to formation of rough undulated surfaces with period of about 300 nm, while the excitement with kilohertz frequency causes smoothening of the films surface [1]. Both effects can be useful in practice for production of active layers in sensorsics, optics, microelectronics, etc.

During our investigations of tellurium films with nominal thickness of 100 nm, deposited by FATEV at input frequency of 4 kHz, an interesting fact was observed - together with the significant smoothening
of the surface (a drop of the root mean square surface roughness $S_q$ from 34 nm (for a film, deposited by conventional PVD) to 14 nm (for a sample, deposited by FATEV with 4 kHz impact) a formation of an ordered columnar structure from the bottom to the top of the film was observed [1].

The aim of the present work is to study the in-depth changes in FATEV deposited tellurium films with nominal thickness of 60 nm, caused by vibrations with input frequencies of 0, 50, 4000 and 10000 Hz. In addition, we will present new data about the thickness effect on the surface morphology of FATEV deposited Te films, which would be useful for widening the knowledge about the possibilities of the FATEV method.

2. Experimental procedures

Series of tellurium (Merck, 5N) films with nominal thickness of 60 nm were deposited using FATEV approach [1, 2] with deposition rate of ~0.5 nm/s during the impact of mechanical vibrations with input frequencies of 0, 50, 4000, and 10000 Hz on Si (100) substrates. The deposition rate and the film thickness during the deposition were controlled using a quartz-crystal microbalance device Miki MSV 1841/A.

SEM observations have been performed using an e-Line EBL equipment in SEM mode (Raith GmbH., Germany), working with an accelerating voltage of 10 kV. The as-deposited Te films were observed on top and cross-section with magnification of 50-, 100- and 200-thousand times.

The optical properties of the films deposited on silicon substrates were examined by UV-Visible-Near IR phase modulated spectroscopic ellipsometric platform UVISEL2 (HORIBA JobinYvon) in the spectral range of 1.5 - 6 eV at 70 ° incident angle.

AFM measurements have been carried out on a scanning probe microscope Multimode V (Bruker, Santa Barbara, CA). The images have been taken in tapping mode, as each sample has been investigated in multiple points of the surface. The measurements in scales of 1 and 3 µm have been performed with scanning rates in the interval of 0.5-2.0 Hz and with an image resolution of 512 lines per scan direction. Al-coated silicon cantilevers TAP150-Al-G (Budget Sensors Innovative Solutions Bulgaria Ltd., Bulgaria) with a nominal resonant frequency of ~150 kHz and spring constant of 5 N/m have been used. The radius of the cantilever’s tip is smaller than 10 nm. The root mean square roughness ($S_q$) of the samples was determined in the scale of 3 µm. The images have been just flattened before the analysis, made with the SPIPtm 6.1.0 program.

The structure of the films was evaluated through grazing incidence X-ray diffraction (GIXRD) using a Rigaku SmartLab X-ray thin film diffraction system (Rigaku Corporation, Japan) at CuKα1,2 irradiation ($\lambda$=1.5418 Å) and an angle of incidence of 0.5 °. The XRD patterns were taken in the Bragg angle (20) range from 10 to 60 ° with a step of 0.01 °.

3. Results and discussion

The XRD patterns of the films are presented in figure 1. The phase analysis of the latter shows presence of a hexagonal tellurium phase, indexed in the JSCPD database under the powder diffraction file (PDF) 101-1098. A change of the main peak from [101], as described in the literature, to [100] is observed, which most probably is caused by the influence of the Si (100) substrate orientation.

The results from the structural analysis of the samples are presented in Table 1. The lattice constants are similar to these described in PDF 101-1098 ($a$=b=4.454 Å, $c$=5.924 Å; $a$=$\beta$=90 °, $\gamma$=120 °). The average crystallites size D and the micro-strain $\varepsilon$ of the samples, revealed by the

Figure 1. XRD spectra of as-deposited films and a reference pattern of Tellurium (PDF 101-1098).
Williamson-Hall method [3], are also presented in Table 1.

| Frequency, Hz | a, Å | b, Å | c, Å | α=β, ° | γ, ° | 2θ, deg | FWHM, deg | D, nm | ε | Sq, nm |
|--------------|------|------|------|--------|-------|----------|-----------|-------|----|--------|
| 0            | 4.457 | 4.457 | 5.908 | 90     | 120   | 22.990   | 0.448     | 17.72 | 0.11 | 7.25   |
| 50           | 4.457 | 4.457 | 5.919 | 90     | 120   | 22.997   | 0.424     | 16.28 | 0   | 9.77   |
| 4000         | 4.453 | 4.453 | 5.914 | 90     | 120   | 23.011   | 0.430     | 16.92 | 0.23 | 3.39   |
| 10000        | 4.459 | 4.459 | 5.922 | 90     | 120   | 23.002   | 0.45(2)   | 16.61 | 0.12 | 4.22   |

The morphological and topological investigations of the surface showed that the films are homogeneous with randomly distributed nanoparticles peaking, whose organization increases with the increase of the frequency of the vibrations applied during deposition. SEM microphotographs visualizing this are presented in figure 2. The surface roughness of the films, determined by AFM and presented in Table 1, follows the pattern, observed for the thicker Te films [1], and decreases with the increase of the vibrations frequency. The cracks, observed on the surface of the sample, deposited at input frequency of 4000 Hz (figure 2c) are most probably due to an increased stress in the films, as also shows the micro-strain value from the XRD evaluations of the same sample (Table 1).

Figure 2. Top view SEM microphotographs of tellurium films deposited at impact of vibrations with input frequencies of a) 0 Hz; b) 50 Hz; c) 4 kHz; d) 10 kHz. Magnification – 50 000x.

Cross-section SEM microphotographs of the films are presented in figure 3. A significant difference in the growth mechanism of the films can be seen, depending on the frequency of the vibrations applied. More particularly, the films deposited by conventional method (0 Hz) and at low frequency of 50 Hz are bulk, homogeneous and without distinct nanoparticles forming the layer, while the films deposited using frequencies in the kilohertz range are consisted of singular nanoribbons growing predominantly towards the z-axis from the very beginning of the film formation. The average widths of the nanoribbons, estimated by averaging of the visible formations from the morphological investigations in both cross-section and top at magnification of 200 000x, are ~ 30 nm for the samples deposited under the impact of 4 kHz vibrations, and ~ 20 nm for those, deposited using 10 kHz input frequency.

In order to reveal a quantitative presentation of these observations, spectroscopic ellipsometry evaluations were performed. In our calculations the samples were modelled either as: (i) an isotropic layer with a top overlayer with variable ratio between the bulk and the void parts caused by surface roughness, called Model 1 in the text below, or (ii) a single porous layer (Model 2). The optical constants of the tellurium films were described by the Tauc-Lorentz dispersion model [4]. Due to the irregular shape of the pores in the thin films (see figure 3), the Bruggeman approximation [5] was applied in the present work for calculation of the void fraction. The validity of the applied models was determined by...
a calculation of a common mean square error function ($\chi^2$), which accounts for the discrepancies between the measured ("meas") indices and simulated ("calc") data for $\psi$ and $\Delta$ for each photon energy value $h\nu$ [4]:

$$\chi^2 = \frac{1}{2N-P-1}\sum_{i=1}^{N} \left[ (\Psi_{calc}(h\nu) - \Psi_{meas}(h\nu))^2 + (\Delta_{calc}(h\nu) - \Delta_{meas}(h\nu))^2 \right]$$

(1)

where N and P are the total number of data points and the number of fitted parameters, respectively.

Figure 3. Cross-section SEM microphotographs of Te films deposited at impact of vibrations with input frequencies of a) 0 Hz; b) 50 Hz; c) 4 kHz; d) 10 kHz. Magnification – 200 000x.

The calculations showed that the best fits for the films, deposited by conventional method and by FATEV at input frequency of 50 Hz, were obtained when Model 1 was applied (figure 4a), while these, deposited at high frequency impact, were described better by a single porous layer (Model 2, figure 4b).

The results from these evaluations, as well as the thickness of the films (determined from cross-section SEM observations), and the root mean square surface roughness $Sq$ (determined by AFM, and shown again here for convenience), are presented in Table 2.

| Frequency, Hz | Model | $d$, nm (bulk layer) | $d$, nm (porous layer) | Te/void ratio, % | $d$ (SEM), nm | $Sq$, nm |
|--------------|-------|----------------------|------------------------|----------------|--------------|----------|
| 0            | 1     | $45.88 \pm 4.16$    | $17.89 \pm 3.42$      | 50/50          | 56.94        | 7.25     |
| 50           | 1     | $59.90 \pm 1.80$    | $17.20 \pm 4.30$      | 44/56          | 60.94        | 9.77     |
| 4000         | 2     | -                    | $69.73 \pm 2.72$      | 86/14          | 63.52        | 3.39     |
| 10000        | 2     | -                    | $68.21 \pm 2.69$      | 84/16          | 66.47        | 4.22     |
The thicknesses and roughnesses determined by the spectroscopy and microscopy methods correspond well when one takes into account that the whole thickness containing pores is defined in the ellipsometry evaluations, while during the AFM and SEM investigations the thickness and the roughness are determined at an average level.

Looking at the porosity estimations it can be concluded that the thin films can be divided in two groups – (1) bulks with highly porous surface layer, and (2) porous layers through their whole volume with average voids content of ~15%.

The observations of the first group are expected and confirm the effects observed in the thicker Te films, investigated previously by us [1]. On the other hand, the presence of determinable pores in the columnar-like tellurium films, deposited using a frequency impact of 4 and 10 kHz, is a new fact, which can be discussed and analyzed.

It has been stated before [1, 2] that the mechanical vibrations with input frequencies in the audio range cause activation of the substrate surface and formation of undulated surfaces with approximate period of 300 nm when frequencies of 50 and 150 Hz were applied. The change of the preferential growth direction, the presence of distinct nanoparticles forming columnar structure and the presence of empty voids between them from the very beginning of the films deposition, all observed in the present study, give us grounds to assume that the width of the nano-formations is limited by the corresponding resonance period of the substrate, caused by the outer mechanical excitement applied. Taking into account the widths of the nanoribbons of ~30 nm and ~20 nm respectively for 4 kHz and 10 kHz excitement, one can assume that these input frequencies cause resonance period with approximately the same length on the substrate.

The development of structures with opened nanopores is of constant interest for practical usage starting from sensors and nanosieves (because of the possibility for selective transmission and/or registration of atoms and molecules with defined dimensions), even to optical devices as waveguides and photonic crystals. The observed presence of straightened nanowires with total amount of 15% pores between them in the present study gives grounds for further investigations on the possibilities for practical usage of both: application of FATEV deposition to other crystalline materials, and possibilities of the FATEV deposited tellurium films. However, it has to be mentioned that the deviation from the straight line observed in both figures 2c,d and 3c,d is most probably due to beginning of influence of the self-resonance of the tellurium nanoribbons, caused by the continuous excitement of the substrate. Probably, this disadvantage could be fixed by decreasing the amplitude of the vibrations during deposition. But, in principle, since these distortions are more distinct for the film, deposited at input frequency of 10 kHz, it can be said that the better sample for purposes which require continuous porosity is that, deposited under 4 kHz frequency impact.
4. Conclusions

Tellurium films with nominal thicknesses of 60 nm were deposited by frequency assisted thermal deposition in vacuum (FATEV) using input frequencies of the vibrational impact of 0, 50, 4000 and 10000 Hz. It has been found through XRD phase analysis that all deposits correspond to a hexagonal tellurium. The structural analysis of the films revealed that the crystalline lattice parameters of the tellurium phase correspond to those described in the literature with a micro-strain varying from 0 up to 0.2 (for the films, deposited at 4 kHz vibrational impact). The average crystallites size was found to be around 17 nm for all samples. The morphological observations on the samples’ surface confirm the FATEV effect determined previously for thicker films - the organization of the particles forming the films increases with the increase of the frequency of the vibrations applied during deposition with a peak of the rms surface roughness at input frequency of 50 Hz.

During the observations in cross-section, a change of the growth mechanism of the films was observed when higher frequencies of 4 and 10 kHz were applied. While the samples deposited without excitation impact and under vibrations with a frequency of 50 Hz were consisted of bulk homogeneous bottom layer and a very well defined roughness layer on top, these deposited using frequencies in the kilohertz range were consisted of singular nanoribbons growing predominantly towards the z-axis from the very beginning of the film formation. A quantitative presentation of these observations was offered through spectroscopic ellipsometry evaluations using two models describing the layers’ organization and a Bruggeman effective medium approximation. The microscopy observations were confirmed by the ellipsometry estimations – the samples are divided in two groups – (1) bulks with highly porous surface layer, and (2) bottom-to-top porous layers with average voids content of ~ 15 %. The latter observations give grounds to assume that the excitation of the substrate with input frequencies in the kilohertz range causes a width limitation of the nanoformations defined by the corresponding resonance period of the substrate.

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