Influence of the thickness on the morphology and sensing ability of thermally-deposited tellurium films

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Abstract. Tellurium films with nominal thicknesses of 30, 90 and 300 nm were prepared by thermal evaporation in vacuum at a low deposition rate of 0.3 nm/s. The morphology evolution with the increase of the film thickness was observed by scanning electron microscopy and atomic force microscopy.

Nanorods with a width of about 40 nm were observed on the thinnest films surface. On the 90 nm thick films, the formations grew in priority in the z-direction to nanoblades with the same width, but a length of about 100 nm. The further increase of the thickness led to an increase of the 2D nanoobjects’ width and length and formation of a stacked nanosheet structure. The surface root-mean-square roughness (Sq) increased with the thickness of the films.

Preliminary investigations of the sensing ability of the as-deposited tellurium films with different thicknesses towards water (H₂O), ethanol (C₂H₅OH), acetone (C₃H₅OH), and ammonia (NH₃) vapors were performed by measuring the vapor-induced changes in the film dark current. The films showed appreciable response only to ammonia vapors; their sensitivity was almost equal for the 30 and 90 nm thick films, and decreased significantly for the film thickness of 300 nm.

1. Introduction

Tellurium is a crystalline semiconductor, whose atoms tend to form polymeric, covalently bonded helical chains, readily packed into a hexagonal lattice through van der Waals forces [1]. Due to this specific nature, many authors reported the formation of various nanoobjects (nanorods, nanotubes, nanobelts, nanoblades, etc.) on the films, using complicated physical or soft chemistry methods [2-4]. It can be assumed that when using rather low deposition rates during the Te film preparation by conventional thermal vacuum evaporation, which is a relatively cheap and accessible method, the condensing film will also form 1D and 2D nanoobjects, thanks to its typical crystalline structure.

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Recently the researchers in almost all scientific areas have been working on fighting the air, water and soil pollution by development of approaches for purification or reutilization of contaminated media, or by elaboration of equipment for quantitative measurements of the pollution extent. The tellurium films have been found appropriate and, thus, have been widely studied in view of resistive sensing of CO, NO₂ and NH₃ pollution [5-9].

Taking into account these two objectives, in this work we explored the thickness-morphology and thickness-sensing behavior of slowly deposited Te films.

2. Experimental procedures

Thin films of Te (purity of 5N) were prepared on Si (100) wafers by thermal vacuum evaporation at room substrate temperature, deposition rate of 0.3 nm/s, residual pressure of 7×10⁻³ Pa, and distance between the crucible and the substrate of 20 cm. The deposition rate and the thickness of the films was controlled using a quartz-crystal microbalance (QCM) Miki MSV 1841/A device, and verified by cross-section scanning electron microscopy.

The morphology of the deposited films was investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The AFM measurements were performed on a Multimode V scanning probe microscope (Bruker, ex. Veeco, Santa Barbara, CA). The images were taken in tapping mode, and each sample was investigated on multiple points of the surface. Measurements at scales of 1, 3 and 10 µm were carried out at scanning rates in the interval 0.5-2.0 Hz, and image resolution of 512 lines per scan direction (l/s.d.) for scales of 1 and 3 µm and 256 l/s.d. for 10×10 µm². Aluminum coated silicon TAP150-Al-G cantilevers (Budget Sensors Innovative Solutions Bulgaria Ltd.) with a resonant frequency of 150 kHz and a spring constant of 5 N/m were used. The radius of the cantilever’s tip is smaller than 10 nm. The root-mean-square roughness (Sq) of the samples surface was determined in a scale of 3 and 10 µm. Before the analysis, the images were only flattened. They were further processed using the SPIP™ 6.1.0 program.

The SEM observations were performed using an e-Line EBL equipment (Raith GmbH., Germany) in a SEM mode with an accelerating voltage of 10 kV. The films were observed on top and cross-section with magnification from 50 to 300,000 times.

The structure of the samples was investigated by X-ray diffraction (XRD) using a Bruker D8 diffractometer with a LynxEye solid-state detector at CuKα irradiation (Ni-filter) and a Bragg angle (2θ) ranging from 10 to 60°.

For preliminary investigation of the films’ potential application as resistive sensors for gas detection, their electrical current was measured in the presence of pollutant’s vapors at room temperature and atmospheric air pressure. The film sensitivity is defined as the ratio of the current change with and without presence of active vapors (I_{final}−I_{initial})/I_{initial}). The measurements were performed on the as-prepared Si/Te structures provided with planar aquadag contacts on the top of the Te surface. The reagents used (deionized water (H₂O), 99.7 % absolute alcohol (C₂H₅OH), p.a. acetone (C₃H₅OH) and p.a. ammonia water (25 % NH₃ in H₂O)) in a quantity of 400 µl were introduced in a heated crucible (placed in the investigation chamber), immediately vaporized and distributed into the chamber volume (1.4 l) using a propeller. The measurement of the dark current change was performed up to saturation of the signal.

3. Results and discussion

A typical XRD pattern of the as-deposited Te films is presented in figure 1. The films consisted of hexagonal tellurium, corresponding to IJPCS powder.
diffraction file No. 04-0554. Some peaks of the silicon substrate appeared, and are marked in the figure. No phase or structural changes were observed with changing the film thickness.

Cross-section SEM microphotographs of as-deposited Te films are presented in figure 2, and the results for the film thickness are given in table 1. The films can be considered as bilayered structures, composed by a loose near-surface part and a relatively dense bottom part. This specificity of the samples causes the observed significant difference between the nominal thickness, defined by the QCM technique at set tellurium density of 6.24 g/cm$^3$ [10], and the actual one $d_{\text{actual}}$, roughly calculated as the sum of the bottom layer thickness $d_{\text{bottom}}$ (determined by SEM) and the sample’s root-mean-square roughness $S_q$ (determined by AFM).

![Figure 2](image_url)

**Figure 2.** Cross-section SEM of Te films with nominal thickness of a) 30, b) 90 and c) 300 nm – magnification of 80 000 times.

| $d_{\text{nom}}$, nm | $d_{\text{bottom}}$, nm | $S_q$, nm (for 3 $\mu$m scan) | $S_q$, nm (for 10 $\mu$m scan) | $d_{\text{actual}}$, nm |
|----------------------|-------------------------|------------------------------|-------------------------------|-------------------------|
| 30                   | 57                      | 7.32                         | 7.25                          | 64                      |
| 90                   | 142                     | 33.9                         | 34.3                          | 176                     |
| 300                  | 530                     | 55.7                         | 56.1                          | 586                     |

The results from the surface morphology observations by SPM and SEM are presented in figure 3. The images, obtained by these techniques, are in a good agreement.

As seen in table 1, $S_q$ is practically the same for scanned areas of 3×3 and 10×10 $\mu$m$^2$, which shows that the surface region of the deposited films is extremely homogeneous. The films become rougher with the increase of their thickness.

The thinnest films are mainly formed by laterally distributed fibers, as some of their ends rise on the surface, appearing as randomly distributed nanorods (figure 3a). In the films with nominal thickness of 90 nm, these nanoobjects grow predominantly in the $z$-direction by forming highly disoriented bundled nanoblades having width of ~40 nm and length of ~150 nm (figure 3b). The further increase of the thickness causes agglomeration of the bundles and formation of nanocrystalline conglomerates with a columnar structure (figure 3c).

The well-developed surface observed of the as-obtained Te-films makes them interesting in view of sensing applications. The results from the investigations on the films’ dark current change during introduction of different vapors are presented in figure 4. All films show a weak response towards water, ethanol and acetone.
Figure 3. SEM microphotographs (magnification of 100 000 times) and 2D AFM images (3 \( \mu \)m scan) of Te films with nominal thickness of a) 30, b) 90 and c) 300 nm.

The weak sensitivity to water allowed us to study the samples’ sensitivity towards ammonia vapors by using a standard 25 % water solution in a quantity of 89 \( \mu \)l/l \( \text{NH}_3 \). A change of the sensitivity with the thickness was observed – it decreased with the increase of the thickness (figure 4).

The highest, almost equal, sensitivity to ammonia was observed for samples with a nominal thicknesses of 30 and 90 nm. This is probably due to their bilayered structure: the highly active nanostructured surface layer allows easy attachment of the ammonia molecules, while the relatively dense bottom part ensures good electrical transport conditions.

The sensing mechanism towards ammonia of the films is based on an adsorption-desorption physical reaction. The desorption process is very slow – it takes more than six hours for the films’ initial current values to be restored.

4. Conclusions
Thin films with nominal thicknesses of 30, 90 and 300 nm were deposited on Si (100) wafers by physical vapor deposition at a low deposition rate of 0.3 nm/s.

The influence of the film thickness on the surface morphology was investigated. Formation of nanorods was observed on the 30 nm films, which grew predominantly in the \( z \)-direction forming 2D
nanoblades on the 90 nm samples. The further thickness increase to 300 nm led to consolidation of the objects and formation of a stacked nanosheets structure.

Preliminary resistive sensing investigations were performed on the prepared Si/Te structures at different thicknesses of the active tellurium film. The investigation of the dark current change in the presence of water, ethanol, acetone and ammonia vapors showed significant sensitivity towards NH₃ only. The highest sensitivity values were obtained for the samples with nominal thicknesses of 30 and 90 nm, while the sensitivity decreased with the increase of the film thickness.

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