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“Cymatics” of selenium and tellurium films deposited in vacuum on vibrating substrates

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ABSTRACT

Amorphous selenium and crystalline tellurium thin films were deposited by frequency assisted thermal deposition in vacuum – a new approach for preparation of thin films based on condensation of the evaporated material on an excited substrate, at which vibrations with audible input frequencies are applied. Frequencies of 0, 50, 150 and 4000 Hz were used. The films crystallographic structure stays intact but an effect depending on the applied frequency was observed. Formation of undulated film surfaces at near infrasonic input frequencies excitement is observed with surface roughness maximum at 50 Hz. The surfaces are highly smooth when a mid-sonic 4 kHz vibration was applied.

1. Introduction

Back in 1967 Dr. Hans Jenny described a phenomenon of vibration, which he called “cymatics”. In brief, cymatics (from Greek: κῦμα - wave) is the study of visible sound co-vibration on the surface of a plate, diaphragm, or membrane, causing formation of regions of maxima and minima in a thin coating of particles, paste, or liquid [1]. The obtained cymatic images depend on both the material used (powder, liquid or gas), and the frequency applied. This puts the question “What would happen if mechanical vibrations with a certain frequency are applied on a substrate during thin films' deposition?”

Recently, Thaillan et al. have published theoretical estimations on this question and have stated that thin films should be influenced by acoustic waves vibrations [2,3]. However, in their work they do not take into account the presence of vacuum during deposition, which is required to facilitate the evaporation and to avoid oxidation of the deposited material.

A widely used and inexpensive physical method for thin films preparation is thermal evaporation in vacuum. Sound cannot be distributed at low pressures, but it can be transferred from an oscillation source to a solid as mechanical vibrations with certain frequency. Taking into account that cymatic changes have been observed on both liquids and gases [1], and the theoretical claims for such changes in solid thin films deposited at normal conditions [2,3], one can expect the films, deposited by thermal deposition in vacuum, to be somehow affected if waves with a certain frequency propagate through the substrate.

Selenium and tellurium are basic semiconductor elements, which, together with sulphur, make the foundations of the widely investigated and used in practice chalcogenide materials. Selenium exists in 3 main allotropic forms – 1 amorphous and 2 crystalline (monoclinic and hexagonal), and at least three more have been claimed [4]. Typically thermally deposited Se thin films at room substrate temperature are amorphous [5]. One can expect that the substrate mechanical vibrations during film deposition could affect the structure and surface morphology of the deposited film. The selenium, thanks to its variety of allotropic phases, is a convenient material for fundamental investigations in this direction and thus helpful towards development of novel frequency substrate modulation approaches for film deposition. On the other hand, tellurium (as well as hexagonal selenium) is a typical crystalline semiconductor, whose atoms tend to form polymeric, covalently bonded helical chains, readily packed into a hexagonal lattice through van der Waals forces [6]. Due to this specific nature of tellurium, many authors report formation of nanorods, nanotubes, nanowires, nanobelts, nanoblades, etc. during thin films' deposition [7–10]. These multiple possibilities of structural formations also could be of great interest towards thin films surface shaping using mechanical oscillations during deposition.

Everything said above gave us reasons to investigate the influence of periodic mechanical vibrations of crystalline Si (100) substrates during deposition on the morphology and structure of Se and Te thin films, prepared by thermal evaporation in vacuum.

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2. Material and methods

Standard equipment for thermal deposition in vacuum was modified by introducing a source of mechanical vibrations with acoustic wave frequency.

A block diagram of the modified equipment is shown on Fig. 1. The base (standard) equipment for the experiments is generally consisted of rotary pump (RP), diffusion pump (DP), vacuum chamber (VC), and Tantalum crucible (Ta-C), connected to electrodes (E). The vacuum level in the chamber is measured by vacuum-meters for low (LV) and high vacuum (HV), and the energy, needed for heating the crucible, is provided through a power supply unit (PS). A source of mechanical vibrations with acoustic wave frequency (LS) – 2 in. 180 mW closed loudspeaker with frequency response in the interval 20–20,000 Hz, is situated perpendicularly to the evaporation flow, and a 2 in. Si (100) wafer (Si-W) is fixed in its corpus. The LS is connected to a sound amplifier (SA). The required sinusoidal frequency signal is generated using a C++ based program and translated towards the SA + LS sound system by a computer (PC).

Thin films of Se (source material with purity of 6 N) and Te (purity of 5 N) were deposited on 2 in. Si (100) wafers, set on the LS face and maintained at room temperature. The oscillations amplitude corresponded to 80% of the maximum LS's output power. Sound frequencies of 0, 50, 150 and 4000 Hz, deposition rate of 0.3 nm/s, and residual pressure under the vacuum chamber of 7.10^{-3} Pa were applied. The distance between the crucible and the substrate was 20 cm. The deposition rate and the thickness of the films was controlled during preparation using a quartz-crystal microbalance system Miki MSV 1841/A, and verified by cross-section scanning electron microscopy (SEM).

AFM measurements were performed on scanning probe microscope Multimode V (Bruker, ex. Veeco, Santa Barbara, CA). The images were taken in tapping mode, as each sample has been investigated on multiple points of the surface. Measurements in scale of 1, 3 and 10 μm have been performed with scanning rate in the interval 0.5–2.0 Hz and images resolution of 512 lines per scan direction (l/s.d.) for 1 and 3 μm scan and 256 l/s.d. for 10 μm scan. Aluminum coated silicon cantilevers TAP150-Al-G and TAP300-Al-G (Budget Sensors Innovative Solutions Bulgaria Ltd., Bulgaria) with nominal resonant frequency of ~150 and ~300 kHz, and spring constants of 5 N/m (soft-tapping mode) and 40 N/m (medium- and hard-tapping mode) respectively, have been used. The radius of the cantilever's tip is smaller than 10 nm. The root mean square roughness (Sq) of the samples was determined in scale of 3 and 10 μm. The images have been just flattened before the analysis. The images were further processed using SPIP^{tm} 6.1.0 program.

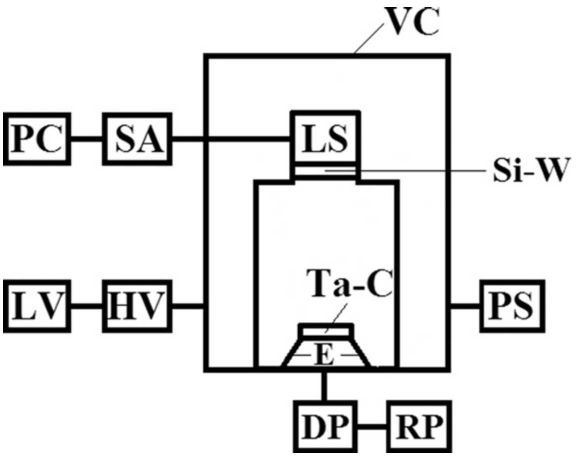

Fig. 1. Block-diagram of the equipment for thermal evaporation in vacuum with built-in system for mechanical vibrations with sound wave frequency. RP – rotary pump, DP – diffusion pump, LV – low vacuum-meter, HV – high vacuum-meter, E – electrodes, Ta-C – Tantalum crucible, PS – power supply unit, Si-W – silicon wafer, LS – loudspeaker, SA – sound amplifier, PC –computer, VC – vacuum chamber.

SEM observations have been made using Nova NanoSEM 630 (FEI, USA) for the selenium films and e-Line EBL equipment in SEM mode (Raith GmbH, Germany) for the tellurium ones. Both equipments are working with accelerating voltage of 10 kV. The Se and Te films were observed on top and cross-section with magnification from 50 to 300,000 times.

The thin films XRD investigations were performed using Bruker D8 diffractometer with LynxEye solid state detector at CuK$_\alpha$ irradiation (Ni-filter) and Bragg angle (2θ) range from 10 to 60°.

3. Results

3.1. Amorphous selenium

First, thin Se films were investigated towards oscillation induced morphological and structural changes.

Atomic force microscopy (AFM) images of as-deposited Se films, prepared at frequencies of the mechanical vibrations generated by the LS source (called from now on input frequencies) of 0, 50, 150 and 4000 Hz, are presented in Fig. 2, and the corresponding root mean square (rms) roughnesses (Sq) for an area of 3 × 3 μm^2 is shown in Fig. 3a.

As it can be seen from Figs. 2 and 3, the mechanical vibrations influence the morphology of the films. The LS provided oscillations with input frequencies in the interval 0–150 Hz, cause appearance of large-scale fluctuations (humps) on the films surface with lateral size of about 300 nm. The rms roughness (Sq) goes through a maximum (Sq = 2.3 nm) at frequency of 50 Hz (Fig. 3a). Significant smoothening of the surface is observed when applying vibrations with frequency of 4 kHz – the Se films, deposited at this frequency are extremely smooth and their Sq is ~0.3 nm.

According to the cross-section SEM observations, no morphological changes related to the applied mechanical vibrations are observed in the films volume – the samples are homogeneous with no presence of pores or crystalline formations. In addition, the applied mechanical vibrations do not cause any structural changes in the samples. The XRD patterns show a plateau (Fig. 4 – gray line), which is typical for amorphous materials, such as selenium.

3.2. Crystalline tellurium

After establishing a relation between the frequency of the mechanical vibrations, applied on the substrate during deposition, and the surface roughness of the amorphous Se samples, thin films of crystalline tellurium were deposited, and investigated towards morphological and structural changes.

Nanoblades (width below 40 nm, and length of around 100 and 200 nm depending on the applied frequency) are observed on the surface of all deposited films (Fig. 5). Such objects are typical for crystalline Te [7–10] and are normally related to the structural peculiarity of tellurium – tendency towards formation of covalently bonded chains. In both types of our samples (deposited without and when applying frequency excitement) the nanoblades observed are extremely homogeneously distributed across the total substrate area (Sq in scale of 3 and 10 μm differs insignificantly – Fig. 3b). The vibration frequency effect is similar to that observed for the selenium films – the rms surface roughness goes through a maximum at frequency of 50 Hz and strongly decreases at frequency of 4 kHz (Fig. 3b).

The variation in the frequency of the mechanical vibrations applied on the substrate causes more significant morphological changes in the Te films when compared with the Se films. As seen from Fig.6a the '50 Hz' films can be considered as a graded structure, formed by highly disoriented ensembles of nanoblades, whose porosity decreases in depth. The ensembles form a large scale undulation on the film surface