SmS THIN FILMS WITH NANOSIZE SURFACE ARCHITECTURE

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Samarium sulfide thin films with thickness in the range from 40 to 100 nm were deposited on vacuum annealed sapphire plates that received ion beam treatment after annealing to reduce surface roughness. The deposited thin films were then subjected to vacuum annealing and ion beam treatment again and films surfaces good enough to use scribing to create nanosize surface elements were obtained. Diffraction grating was then prepared with the aid of a diamond coated cantilever and examined using electric force (EF) and magnetic force (MF) modes of atomic force microscope (AFM). The prepared grating was shown to have semiconducting channels between the metallic grooves separated from one another by 100 nm distance. The disclosed distinct properties of the grating are discussed in terms of variable valence of Sm ions. It is figured out that SmS thin films are very promising as materials to scribe on and obtain desirable surface architecture.

Keywords: Atomic Force Microscopy, SmS polycrystalline film, nanoscale structures, diffraction grating, Magnetic Force Microscopy, Electric Force Microscopy.
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1. INTRODUCTION

Phase-change materials revolutionized media industry by providing inexpensive, high-speed, portable and reliable platform for vast volume data storage. Such a great application became possible due to semiconductor-to-metal phase transition that dramatically changes all their physical properties, allowing eventually to controllable switching between two stable states. This work is addressed to feasibility of using the rare-earth based phase-change material such as SmS to obtain multifunctional elements at the nanoscale. The idea underlying the work originates from variable valence of Sm, that leads to semiconductor-to-metal phase transition in SmS under mechanical deformation.

SmS advantageously differ from other semiconductors in that metallic state is reached in this material under quite low external pressure. It has recently become clear [1] that SmS polycrystalline films exhibit cluster structure. The cluster sizes in SmS films vary within 5 -100 nm, depending on film growth conditions and after-growth treatment. A semiconductor-type conductivity is observed for cluster larger than 20 nm. On the other hand, conductivity is metallic when cluster size is below 20 nm [1]. SmS is known as n-type cubic semiconductor with lattice parameter a=5.97Å at room temperature [1]. SmS shows semiconductor-to-metal phase transition under pressure due to the change of the valence of Sm ions from Sm^{2+} to Sm^{3+} +e [2]. Normally, 4f-levels of Sm^{2+} ions positioned in the knots of the crystal lattice of SmS are 0.23 eV below the conduction band bottom. However, they move at a rate of 0.16 meV/MPa towards conduction band bottom under compression and enter conduction band.

According to model calculations [3], the pressure of phase transition into metallic state is more than 1000 MPa and 650 MPa for thin film and bulk material, respectively. Heating of the polished (and, hence, partly metallic) SmS samples up to 500 -600 K leads, as observed [4], to reversible change back to completely semiconducting phase. Note that voltage emerging during such heating performed in the absence of temperature gradients [5] is indicative of concentration gradients caused by Sm excess against its stoichiometric concentration.

2. PREPARATION DETAILS

2.1 Thin film and diffraction grating preparation

We used thermo-vacuum deposition technique [2] to obtain SmS submicron thin films. In our case substrate temperature was 600 C while deposition from target occurred at 2500- 2700 C. Film thickness was monitored during deposition using well-known piezo-plate method [6].

It is straightforward that substrate selection is very important for obtaining homogeneous thin films of such a "gentle" material like SmS. The main criterion for selection is possibly small lattice mismatch between substrate and samarium sulfide. Besides, surface roughness of the used substrate shall be negligible. As our observations have shown, unfulfilling of either of the above two conditions results in inhomogeneous SmS thin films due to local mechanic deformation.

We used sapphire substrates which were preliminary annealed at 1500ºC during 4 hours.

After annealing, substrates received ion treatment for 2 hours in addition. Above annealing and ion cleaning were repeatedly performed unless surface roughness of the substrates was down to 6 nm.

Thickness of the SmS thin films obtained on sapphire substrates was within 40 - 100 nm. Annealing at 600ºC followed SmS thin film deposition. Perfection of the annealed films was examined using *X*-ray diffraction technique by means of a XRD D2 PHASER (Bruker, Germany). Surface topography of the films was studied using atomic force microscopy system AFM SmartSPM™ with

measuring head AIST-NT. Resonance frequency of diamond cantilever was 305.6 kHz.

Fig. 1 (a) and 1 (b) show topographic images of sapphire substrate and SmS film deposited on this substrate, respectively. Surface roughness of the substrate is below 6 nm while that of SmS film is below 3 nm. We used scribing method [7] to prepare diffraction grating on the surface of SmS thin films. The parameters such as scribing rate, depth etc. were varied in accordance with preliminary estimations done with allowance for relevant properties of thin film and cantilever materials.

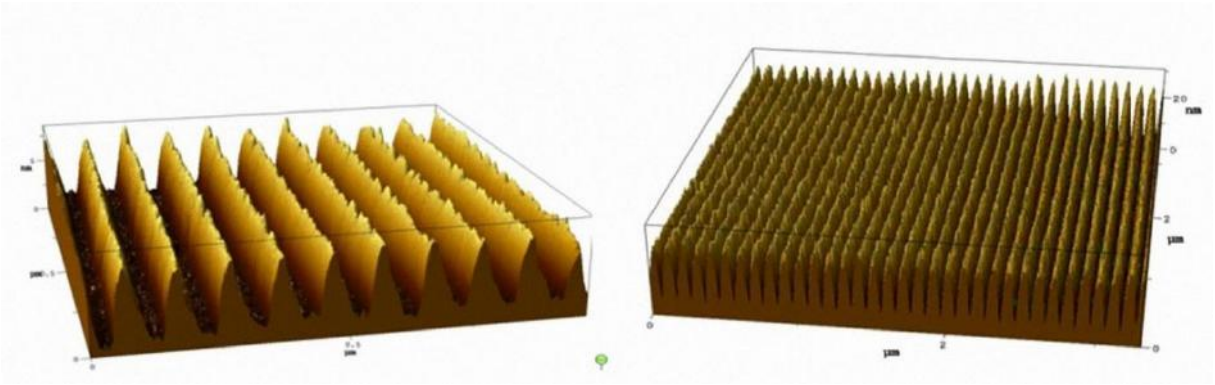

Fig. 1. "Diffraction lattice" type nanoelements on the surface of nanothickness SmS.

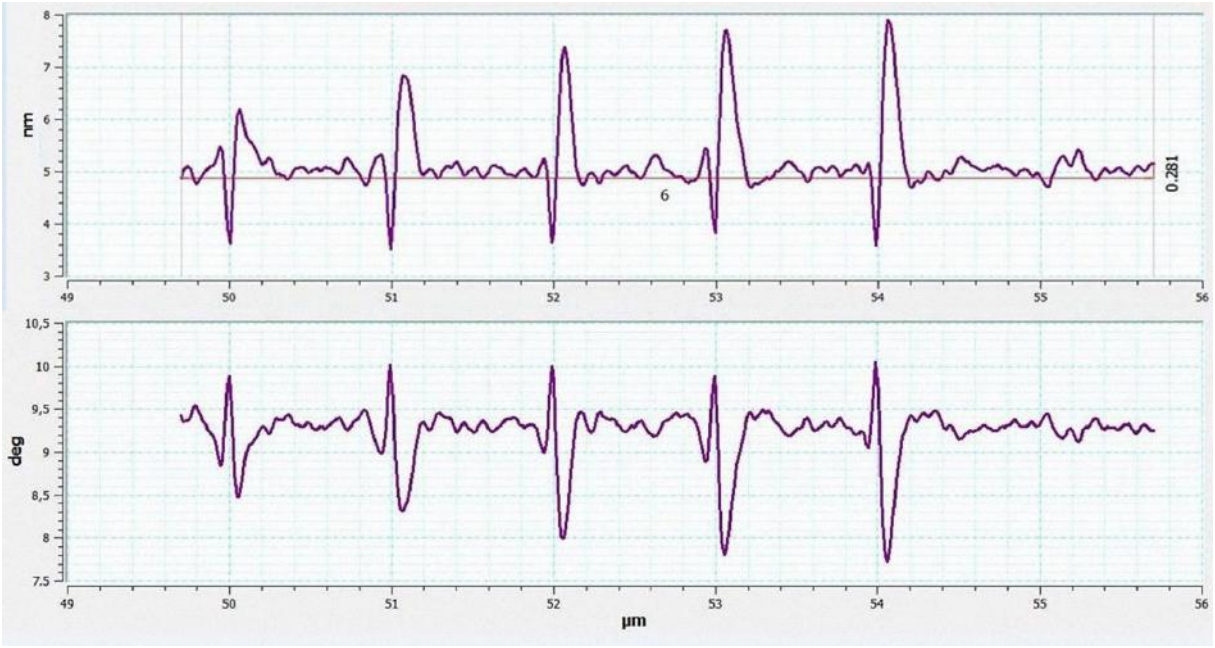

Fig. 2. The topographies of the profiles of SmS sample surface received by the two-pass technique. The profile of topography of the surface with the applied grooves is given in the top chart. In the bottom chart is given the amplitude-phase contrast of the resonant fluctuations of the probe.

3D images of the diffraction grating obtained on the surface of the synthesized SmS films are shown in fig. 2. The images belong to the same grating.

The total area of the obtained grating is up to $10x10\mu m^2$. The groove frequency is 10 μm^{-1}, the scribing depth is from 10 to 20 nm (by about 15 nm).

3. ELECTROSTATIC FORCE AND MAGNETIC FORCE MICROSCOPES

Electrostatic Force Microscopy (EFM) and Magnetic Force Microscopy (MFM) we applied in this work were based on two-pass contactless measurements. Surface topography was taken in the first pass and second pass in which vibrating cantilever remained at constant height while moving above the surface allowed to obtaining a map of electrostatic or magnetic interaction between cantilever tip and surface under consideration.

3.1 Electrostatic Force Microscopy profile

Fig. 3 (top part) displays topographic profile of the grating with grooves separated from one another by 400 nm distance. This grating with low groove frequency was specially prepared for EFM studies to avoid possible electrostatic influence of the grooves on each other. Fig.4 (bottom part) shows the

amplitude-phase contrast for resonance vibrations of the cantilever tip. It is clearly seen that inter-groove regions show no change in signal. Note that any change in signal's amplitude or phase is determined in this case by the first derivative of the electrostatic interaction between surface and cantilever (8).

The obtained profile of the amplitude phase-contract witnesses that scribing with resultant grating creation leads to the ordered electrostatic field distribution that reflects ordered concentration gradient of the charged particles. This gradient is supposed to emerge due to partial metallization of the SmS surface after scribing. More exactly, the surface edges of the grooves are metallic while regions between the grooves remain semiconducting. Shown in fig. 5 and supports above assumption regarding partial metallization of SmS. According to our estimations, the concentration of Sm ions that raised their valence to 3+ is approximately 90 cm $^{-3}$ per 1nm groove length.

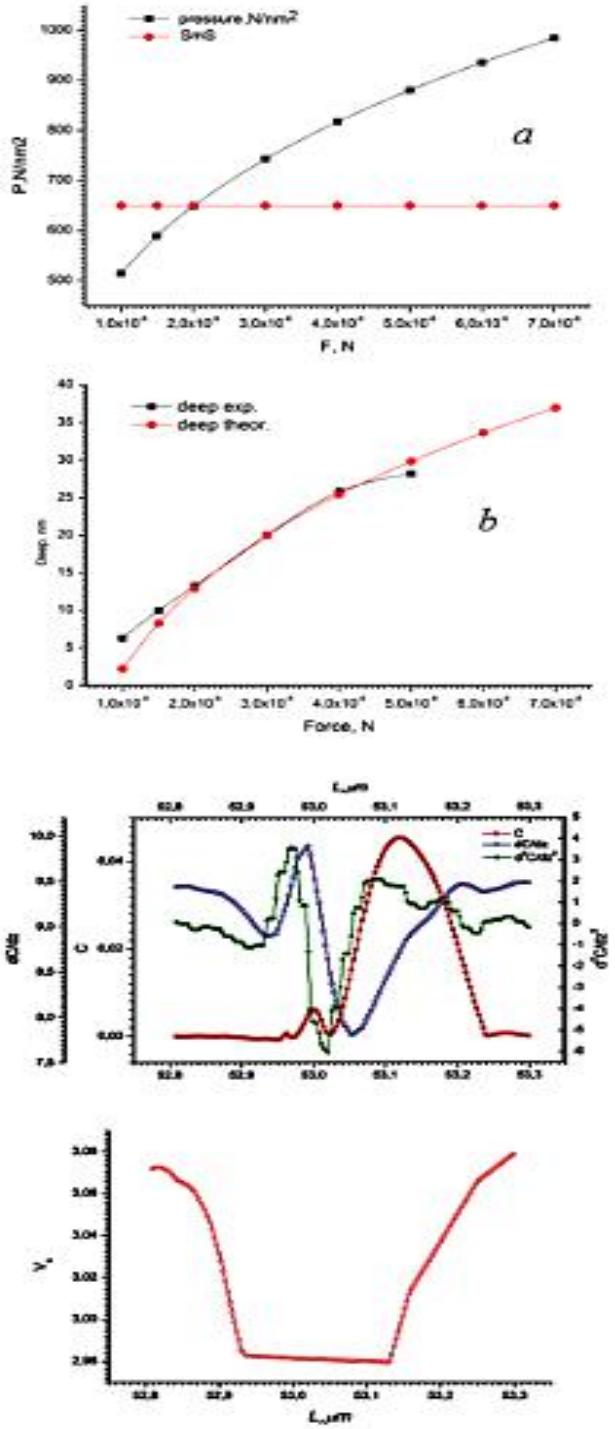

Fig. .3. a - dependence of electrostatic force on "z" distance of the tip provision to SmS film surface; b - determination of the activation energy magnitude at the set mode of dicing; c – three components of force of interaction cantilever- SmS film; d -the established E_c profile after groove dicing Using calculations data (fig. 2, and 4 a), and also experimental

data (fig. 6, b) of activation energy changes for thin polycrystalline SmS films, the optimum mode (fig. 4 is established, b) of grooves dicing of the diffraction lattice (fig. 3) was set.

3.2 Magnetic Force Microscopy profile

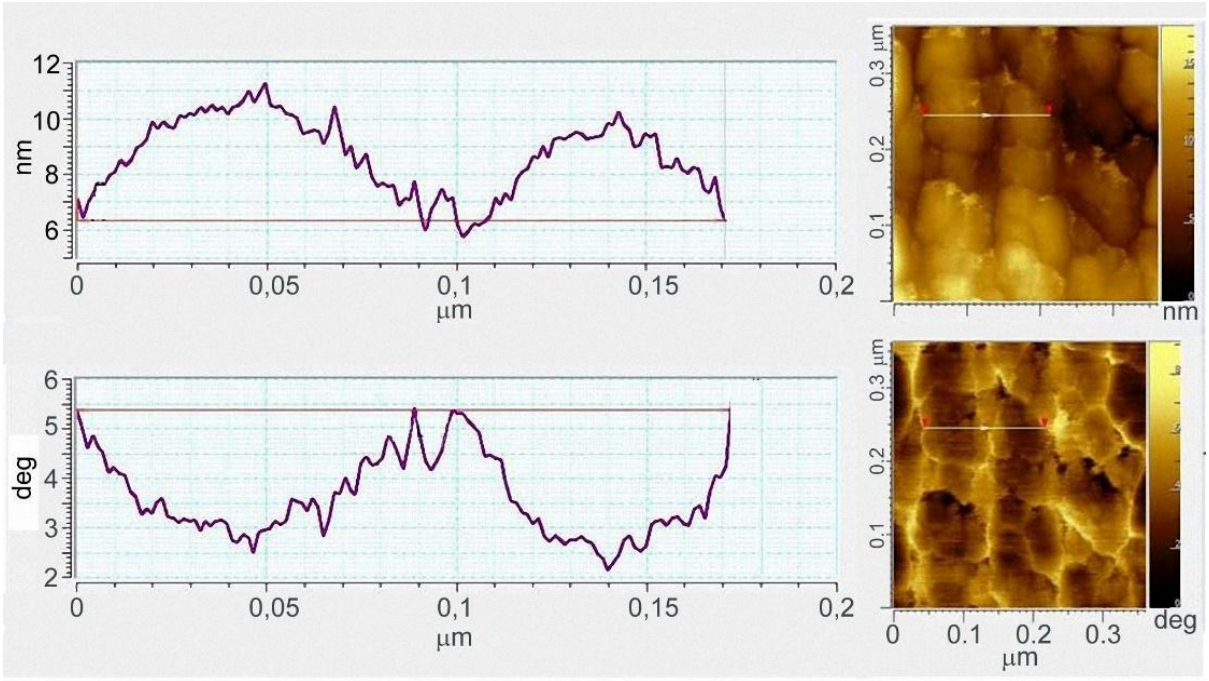

Fig. 4. 2D profiles of the sample surface of samarium sulfide: a – surface topography; b – the MFM profile of the surface.

It is known that magnetic susceptibility of semiconducting SmS is practically independent of temperature [9], which is typical for paramagnetic materials [10]. Magnetic susceptibility of metallic SmS is lower in comparison with semiconducting phase [4], which is caused by transition of Sm2+ ions into Sm3+ state [9]. AFM and MFM data for the grating shown in fig. 3 are given in fig. 6. The data were obtained using Pt coated Co-Cr cantilever with resonance frequency 160 kHz. It is well known that any contrast in MFM images reflects change in sample magnetization [11]. Comparison of periodic oscillations in topographic 2D profile (fig. 6, top part) with those in MFM 2D profile (fig. 5, bottom part) just witnesses that groove's edge is interacting with the tip of Co-Cr cantilever weaker than groove's depth. This is completely consistent with the fact that magnetic susceptibility of the metallic SmS is smaller than that of the semiconducting SmS. To overall, MFM data, along with previous EFM data are unambiguous regarding the co-existence of semiconducting and metallic phases in gratings prepared by scribing the surface of SmS thin films.

4. CONCLUSION

We have managed to prepare nano-dimensional diffraction grating on the surface of SmS thin film, thus showing that this material can be used for creation of desirable surface architecture by scribing. Besides AFM, we have also performed EFM and MFM characterization of the obtained gratings that have been shown to be two-phase structures with metallic edges separated by semiconducting channels. In fact, the distinct feature of the obtained structure is simultaneous presence of purely geometric modulation and spatial modulation of electric and magnetic properties. This might be useful for development of multifunctional logic elements at the nanoscale.

ACKNOWLEDGEMENTS

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