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Growth of surface relief structures on Ag/AsS_2 bilayer thin films by electron beam irradiation

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ABSTRACT

Metal/chalcogenide thin films have a great potential for the application in electronics and microelectromechanical systems. Methods of creating different surface relief structures on metal/amorphous chalcogenide (Ag/AsS_2) thin film bilayer surface by using focused electron beam were explored in this study. Ag/AsS_2 bilayer was prepared in two steps – (1) Ag thin film was sputtered on a substrate by DC magnetron sputtering method and (2) AsS_2 thin film was deposited on Ag thin film surface by thermal evaporation method. Using EB in scanning electron microscope, two types of surface relief structures were obtained on the surface of Ag/AsS_2 bilayer: nanodots and micro-squares. The obtained structures were measured by atomic force microscopy. Changes in chemical composition during EB irradiation were observed by energy dispersive spectroscopy. The height of the obtained nanodots was up to 120 nm and the width at half height was up to 230 nm. The height of the middle area of micro-squares was up to 60 nm and additional structure growth was observed along the edges of micro-squares.

1. Introduction

Metal/chalcogenide systems are interesting because of metal migration within amorphous chalcogenide matrix due to photo-diffusion, applied electric field or influence of electron beam (EB). This effect is used for the fabrication of high resolution X-ray masks [1,2] and for operation of microelectromechanical devices [3], programmable metallization cells [4], memory devices [5], fluid control at micrometre scale [6]. Besides metal/chalcogenide systems are used in photonics [7] and plasmonic biosensors [8]. Photo-induced diffusion of metal in chalcogenide thin films has already been researched quite well [9,10], but there are still very few publications about the effect of EB on metal/chalcogenide systems. Furthermore, the effect of Ag diffusion in amorphous chalcogenide matrix can be used for memory devices, while the creation of surface relief structures on metal/chalcogenide bilayer can be useful for fabrication of plasmonic biosensors.

Fitzgerald [11] has recently presented a possible explanation for the formation of line and square patterns in metal/chalcogenide bilayer by EB irradiation in raster or line scanning modes. A chemical reaction occurs between the metal (Ag) and amorphous chalcogenide (a-AsS_2) layers followed by formation of silver sulphide (Ag_2S) layer. Ag_2S is a superionic conductor and is particularly sensitive to focused EB irradiation. EB displaces Ag^+ ions from Ag_2S layer by action of radiolysis and generates secondary electrons. As EB moves along the surface, temperature gradient is generated between the cooling impact on the surface and the higher temperature silver chalcogenide interior. Ag^+ ions move towards cooler surface along temperature gradient and are neutralized by secondary electrons, forming atomic silver aggregates on the surface of the bilayer.

It has been recently shown that it is possible to grow nanodots on metal/chalcogenide bilayer with focused EB [12]. This method allows direct growth of nanostructures on the surface of a sample without additional fabrication steps.

The first aim of this work is to obtain various surface relief structures on Ag/AsS_2 bilayer by EB irradiation; the second is to study how EB parameters affect size and shape of obtained relief structures.

2. Materials and methods

Two Ag/AsS_2 bilayers were prepared in few process stages (Table 1). Two kinds of substrates were used for bilayer preparation. For the first bilayer, which was prepared for irradiation in point mode, BK7 glass was used as a substrate. For the second bilayer, which was prepared for irradiation in raster scanning mode, silicon wafer (Si) was used as a substrate in order to allow electrons to leave the bilayer more easily and to avoid problems due to charge accumulation in the bilayer.

For both bilayers, the first layer (Ag metal layer) was obtained by DC magnetron sputtering technique at deposition rate of 40 nm/min. The thickness of Ag layer was 400 nm in both cases. The second layer (AsS_2 amorphous chalcogenide layer), obtained by conventional vacuum thermal evaporation technique, was deposited on the top of Ag

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Table 1
Parameters of surface relief structures growth.

Parameters	Bilayer 1	Bilayer 2
Type of substrate	BK 7 glass	Silicon wafer
Thickness of layers	Ag – 400 nm	Ag – 400 nm
	AsS_2–90 nm	AsS_2–360 nm
Irradiation mode	Point mode	Raster scanning mode
EB parameters	$U = 30$ kV	$U = 30$ kV
	$I = 2$ pA	$I = 300$ pA
	$d = 14$ nm	$d = 210$ nm
	$t = 20 \div 90$ s	$t = 1 \div 10$ min
Type of surface relief structures	Nanodots	Micro-squares

metal layer (Fig. 1). For the first bilayer, thickness of AsS_2 layer was 90 nm and for the second bilayer it was 360 nm. Deposition rate of AsS_2 layer was approximately 10 nm/s in both cases.

The thickness of thin films was controlled by measuring the mass using a quartz crystal detector. The chemical composition of samples was determined by energy-dispersive spectrometry (EDS), using an Oxford Instruments INCA x-act X-ray detector attached to TESCAN-VEGA LMU II scanning electron microscope. Beam current was 300 pA and the voltage - 30 kV. Acquisition time for EDS measurement in the 20 × 20 microns area was 60 s. The roughness of thin films and structures size measurements were performed by the Park NX10 atomic force microscope (AFM) in non-contact mode. The tip diameter of AFM probe was 10 nm.

Surface relief structure growth experiments were carried out on the bilayers by EB in scanning electron microscope at room temperature, with the accelerating voltage of $U = 30$ kV. Nanodots were obtained using focused EB operated in point mode. EB current I was 2 pA and EB spot size, d, 14 nm. Irradiation time (t) was in the range of 20 to 90 s. Whereas, micro-squares were obtained using EB raster scanning mode. EB current I was 300 pA and EB spot size, d, 210 nm. Irradiation time t varied from 1 to 10 min. The size of micro-squares was in the range of 6.25 to 400 μm^2. Raster scan period time (T) during micro-square growth was 1.5 s. Structures of different sizes were grown by changing irradiation time t.

3. Results and discussion

Nanodots were grown on the surface of Ag/AsS_2 thin film through irradiation with focused EB in vacuum at room temperature and their size depended on the irradiation time. Fig. 2 shows the AFM line scans and AFM 3D image of the nanodots grown with different exposition times.

Nanodot height and width at half height (WHH) show linear dependences on the energy delivered by EB (Fig. 3.). Nanodot height was measured as a distance from sample surface level to nanodot peak, and nanodot WHH was measured as a width at half-height level of the nanodot. EB dose (D) used to grow the nanodot was calculated as $D = I \cdot U \cdot t$, where I is electron beam current, U is electron accelerating voltage, and t - exposition time.

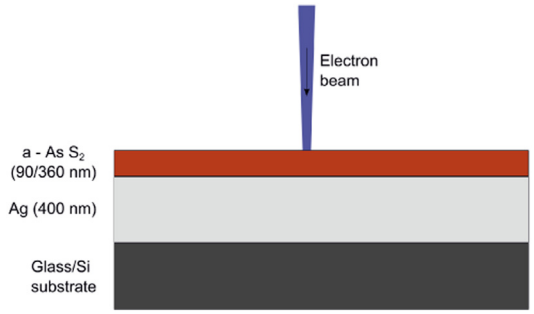

Fig. 1. Schematic of Ag/AsS_2 bilayer and nanostructure growth process.

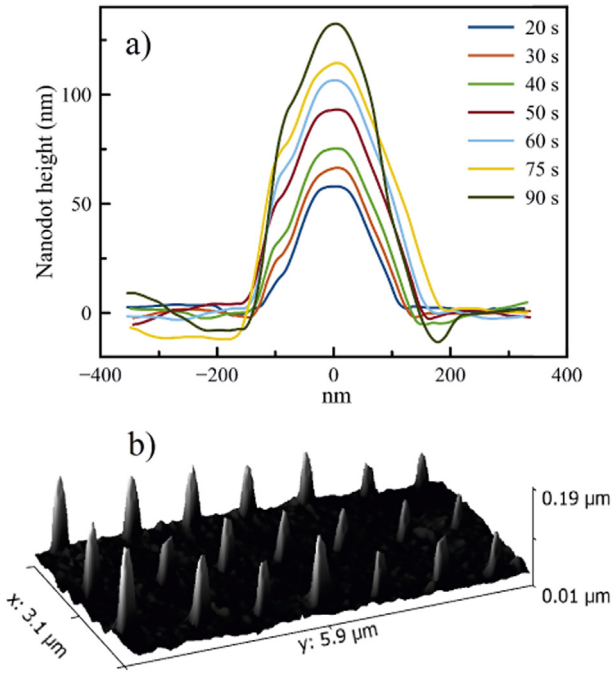

Fig. 2. a) AFM line scans of nanodots grown on the system [glass substrate/Ag (400 nm)/AsS_2 (90 nm)] surface with EB parameters of U = 30 kV, $I = 2$ pA, d = 14 nm, and varying exposition time. b) 3D AFM image of nanodots obtained with the same parameters and exposition time in the range of 20 to 90 s.

The mechanism of nanostructure growth in metal/chalcogenide bilayer, which was discussed in the introduction, is not sufficient to explain the growth of nanodots under EB irradiation in point mode. EB is not moving along the surface of the bilayer during the growth of nanodots, therefore temperature gradient should be mostly perpendicular to surface normal of bilayer. As for temperature gradient, which is parallel to surface normal of bilayer, it seems more likely that the substrate is acting as a cooling surface, because above the surface of bilayer there is a vacuum, acting as a heat insulator. If Ag^+ ions were moving solely because of heat gradient, diffusing away from areas with higher temperature, Ag^+ ions would be moving away from EB and nanodots would not grow on the surface of bilayer. We believe that the electric field, which is formed by focused electron beam, is the main reason for nanodots growth on metal/chalcogenide bilayer as illustrated in Fig. 4. High density of negative charges in focused EB creates the electric field around EB. Positive Ag^+ ions, which are displaced from Ag_2S and Ag layers by action of radiolysis, travel along the electric field lines

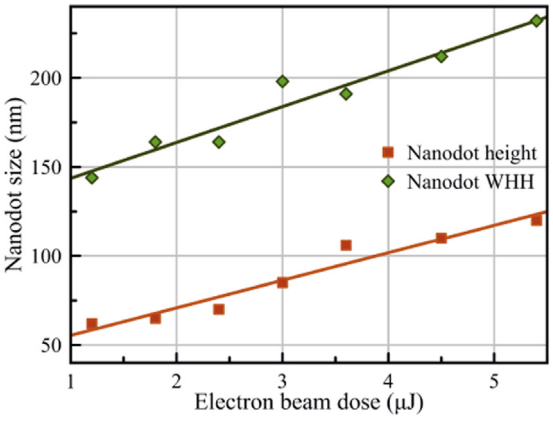

Fig. 3. Dependence of nanodot height and WHH on EB dose in the system [glass substrate/Ag (400 nm)/AsS_2 (90 nm)].