Laser treatment of Se/Bi heterostructure: Bi_2Se_3 nanofilm formation

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Laser treatment of Se/Bi heterostructure: Bi_2Se_3 nanofilm formation

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Abstract. Thin films of Se/Bi heterostructure were obtained by the by thermal vaporization of Se and Bi powders in a vacuum camera. A focused He-Ne laser beam at 632.8 nm is shown to cause local darkening of Se/Bi heterostructure at incident power densities above 3.5 kW/cm^2. The possibility of laser recording of diffraction grating by this technique is demonstrated. It is shown that the resistance between the electrical contacts on the heterostructure reduces as the lines between these contacts are recorded. Data obtained from Raman spectra before and after laser treatment indicate that the darkening is accompanied by Bi_2Se_3 formation.

1. Introduction

Bismuth selenide is a thermoelectric material, possessing features of topological insulator [1,2]. Due to the unique properties Bi_2Se_3 is considered as a promising material for applying in different thermoelectric devices, photosensors, as well as in spintronics, optoelectronics, magnetoelectronics and quantum computation [1,3]. Bi_2Se_3 films could be produced by chemical deposition [4], chemical reaction of sequentially deposited ionic layers [5], electrochemical deposition [6], molecular-beam epitaxy [7], reactive evaporation [8], as well as by organometallic chemical deposition [9]. It was also shown that bi-layer nanofilms, such as Se/Cu, Se/In, Se/Ag and Cu(Ag)/Se, formed on a glass substrate at room temperature could spontaneously and explosively transform into crystalline CuSe, InSe and Ag_2Se nanofilms [10–13]. By analogy with that it was expected that spontaneous crystallization would be observed in Se/Bi heterostructure too. However it does not occur, therefore it is interest to study the crystallization process in Se/Bi heterostructure during local laser heating. Besides that, this study is relevant in terms of development of laser image recording techniques, i.e. for obtaining different diffractive optical elements, all kinds of scales and gratings of optical devices, limbs, matrixes [14–19]. Thus, this work is aimed to study the formation of Bi_2Se_3 nanofilm by laser treatment of Se/Bi heterostructure.

2. Experimental details

Se/Bi heterostructure was formed both on an interelectrode gap of contact pads on a glass substrate (see Figure 1) and on a smooth glass substrate by consecutive thermal vaporization of initial Se and Bi powders in vacuum camera, with the substrate temperature being of 300 K. The contact pads with the interelectrode gap of 0.3×0.5 mm^2 were obtained by mask technology and represent itself bi-layer metal films Cr/Au. Evaporation of samples of initial components of Se and Bi was carried out from tantalum and molybdenum evaporators respectively. The samples were weighed with an accuracy of 0.01 mg. The thickness of Se and Bi layers was measured to be 141 and 45 nm respectively by ellipsometric method.

Thermal treatment of the Se/Bi sample obtained on a smooth glass substrate was implemented by vacuum camera at 10^{-3} Pa and temperature of 493 K. Laser modification of Se(141 nm)/Bi(45 nm) heterostructure was carried out by focused He-Ne laser radiation at 632.8 nm. The Raman spectra of the films were measured by Raman spectrometer (Horiba HR800) at excitation of 632.8 nm before and after laser modification. To avoid thermal effect while Raman studying, the intensity of laser beam focused by 100× objective did not exceed 0.1 kW/cm^2 [18].

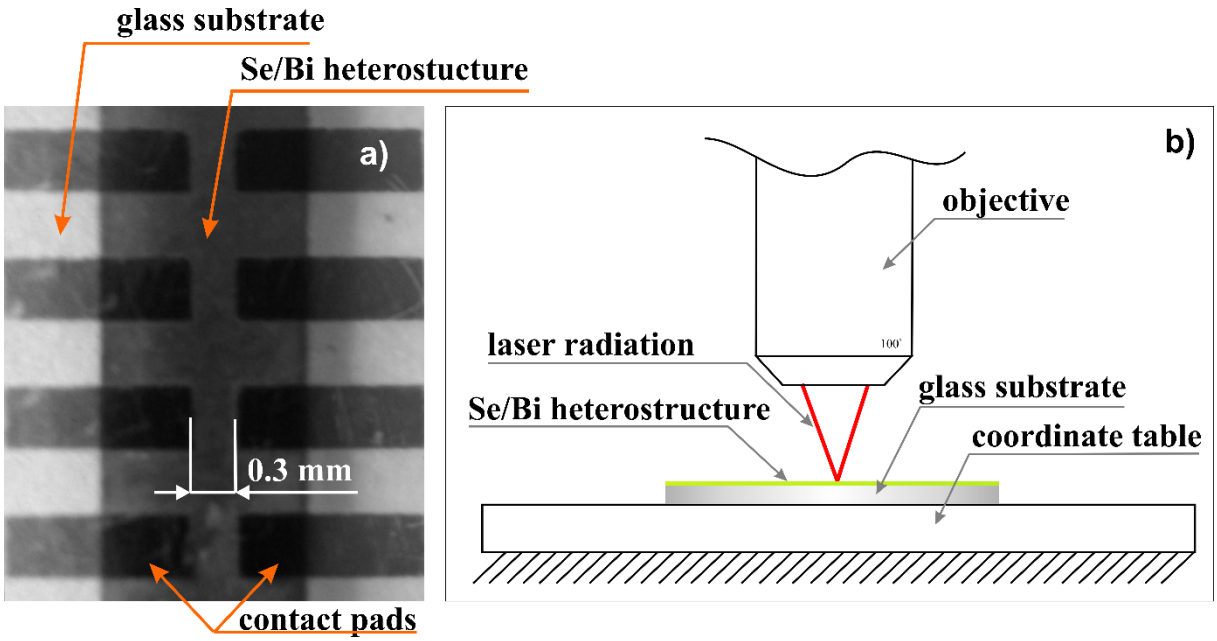

Figure 1. (a) Se/Bi heterostructure formed on an interelectrode gap of contact pads on a glass substrate, (b) sketch of the experiment of laser image recording on Se/Bi heterostructure.

3. Results and discussion

Research into the laser treatment of Se(141 nm)/Bi(45 nm) heterostructure showed that the irradiation of the heterostructure by >3.5 kW/cm^2 laser beam focused by 100× objective led to dark spot formation on the sample surface. With the mechanical laser shutter open, displacing the film using horizontal coordinate table a continuous line can be drawn. The scheme of this experiment is shown in Figure 1b and a set of such lines is presented in Figure 2.

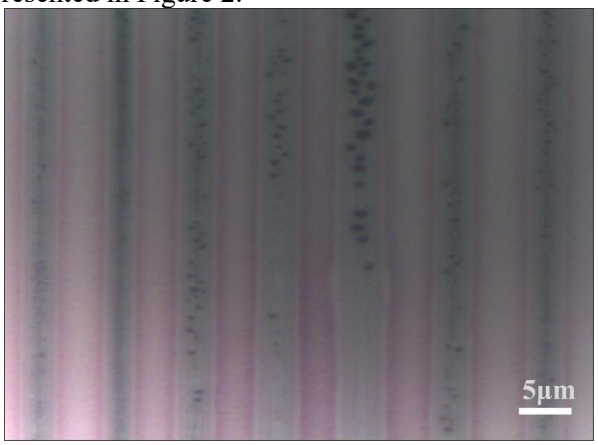

Figure 2. A set of lines drawn on Se(141 nm)/Bi(45 nm) heterostructure by 632.8 nm laser beam focused by 100× objective.

The Raman spectra of the film area before and after laser treatment are presented in Figure 3. The Raman spectrum before laser treatment shows the peaks at 72 and 97 cm^{-1}, assigned to the E_g and A_{1g} Raman modes of bismuth, respectively [20]. These peaks are expected since the upper layer of Se/Bi heterostructure is bismuth. After laser treatment the Raman spectrum shows the peaks at 71, 131 and 173 cm^{-1}, assigned to the A_{1g}^1, E_g^2, and A_{1g}^2 vibrational modes of bismuth selenide, respectively [21].

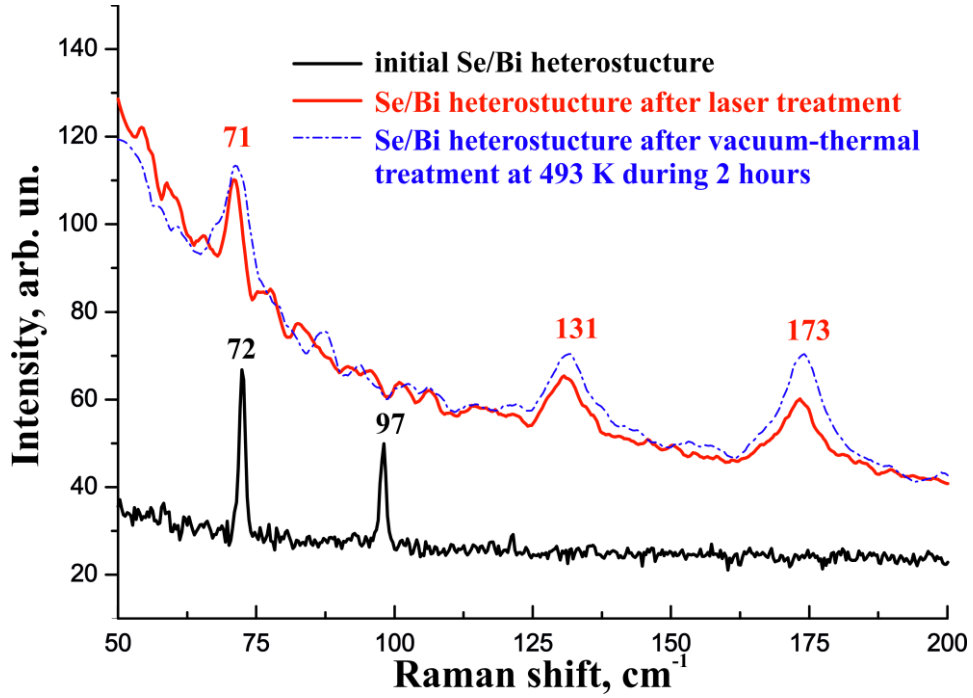

Figure 3. Raman spectra of an area of Se(141 nm)/Bi(45 nm) heterostructure (solid black line) before, (solid red line) after laser treatment, excitation wavelength of 632.8 nm, and (dashed blue line) after vacuum thermal annealing at 493 K during 2 hours.

The obtained results are explained by local laser heating of the heterostructure leading to Bi_2Se_3 film formation in the laser exposure area. Indeed, the Raman spectrum of the sample after annealing at $T = 493$ K during 2 hours consists only of above mentioned vibrational modes assigned to bismuth selenide (see Figure 3, dashed blue line). This indicates on the Se/Bi heterostructure conversion into Bi_2Se_3 during the annealing process and proves that local heating of the Se/Bi heterostructure leads to Bi_2Se_3 film formation.

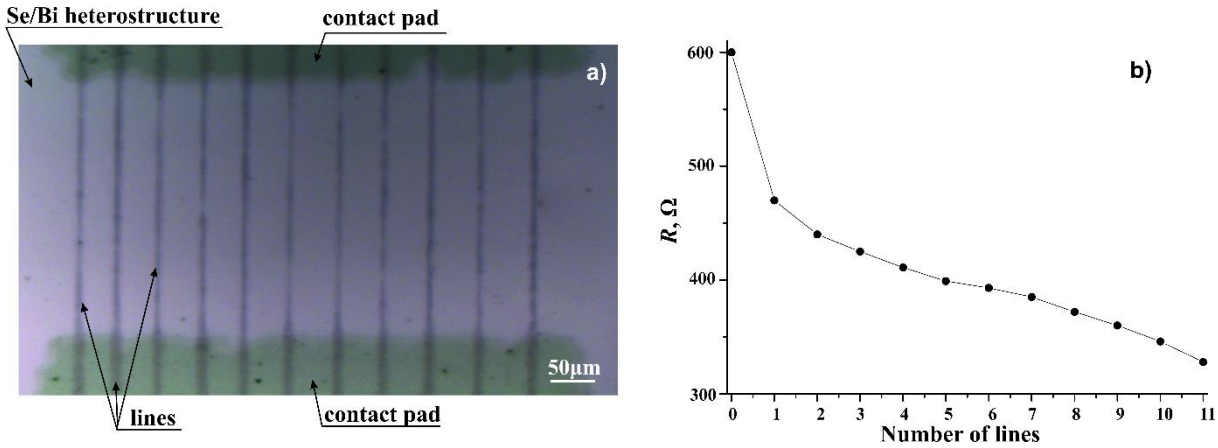

Figure 4. (a) A set of lines drawn on Se(141 nm)/Bi(45 nm) heterostructure formed between contact pads by 632.8 nm laser beam focused by 10x objective, (b) electrical resistance as a function of

number of lines drawn on Se(141 nm)/Bi(45 nm) heterostructure by 632.8 nm laser beam focused by 10× objective.

In Figure 4a a set of lines drawn on Se(141 nm)/Bi(45 nm) heterostructure formed between contact pads by 632.8 nm laser beam focused by 10× objective is presented. The electrical resistance *R* between contact pads as a function of lines number is shown if Figure 4b. One can see that the resistance *R* drops down as the first line is drawn. Then it monotonically reduces with increasing the lines number. Thus, increase of Bi_2Se_3 content between contact pads in Se/Bi heterostructure promotes the electrical resistance reduce.

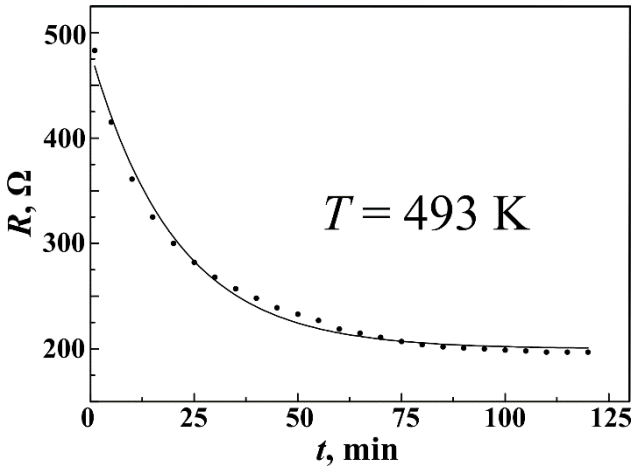

Figure 5. Electrical resistance as a function of annealing time of Se/Bi heterostructure at $T = 493$ K (dots – experiment, line – approximation).

As it was mentioned above, annealing the Se/Bi heterostructure at $T = 493$ K during 2 hours leads to formation of Bi_2Se_3 film as well. The electrical resistance as a function of annealing time of the heterostructure shown in Figure 5 suggests that this process proceeds exponentially following to the equation: $R = R_{in}\exp(-t/\tau)+R_{fin}$, where R_{in} = 281.5 Ω, R_{fin} = 200 Ω, and the characteristic time of equilibrium state establishing τ = 20.5 min (see Figure 5).

Figure 2 and Figure 4a demonstrate that the Se/Bi heterostructure transformation into Bi_2Se_3 under laser radiation is accompanied by increase of the film optical density. Figure 4b and Figure 5 show that the mentioned phase transformation leads to the surface film resistance reducing, i.e. to increase of the film conductivity. These results are in agreement with each other since an increase of a medium optical density is accompanied with an increase of its conductivity and vice versa: a reduce of a medium optical density leads to reduce of its conductivity [22]. It is evident that increase of Se/Bi heterostructure optical density under focused laser radiation can be used for formation of optical images, e.g. for obtaining diffractive gratings. It is well demonstrated by the images of diffractive gratings presented in Figure 2 and Figure 4a. To increase the contrast of the diffractive gratings obtained it is necessary to apply chemical etching techniques, the study of which goes beyond the scope of this work.

4. Conclusions

Thus, we have studied laser influence on Se(141 nm)/Bi(45 nm) heterostructure. Laser treatment leads to local laser heating which causes Bi_2Se_3 film formation in the laser exposure area. Increase of Bi_2Se_3 content in the Se/Bi heterostructure promotes the electrical resistance reduce and leads to increase of the film optical density. The Se(141 nm)/Bi(45 nm) heterostructure conversion into Bi_2Se_3 during the annealing process proceeds exponentially, with the characteristic time of equilibrium state establishing being of 20.5 min. The results obtained show the possibility of laser image recording on thin films of Se/Bi heterostructure.

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