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Formation of surface nanolayers in chalcogenide crystals using coherent laser beams

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ABSTRACT

We have shown a possibility to form laser modified surface nanolayers with thickness up to 60 nm in some ternary chalcogenide crystals (Ag_3AsS_3, Ag_3SbS_3, Tl_3SbS_3) The laser treatment was performed by two coherent laser beams split in a space. As the inducing lasers we have applied continuous wave (cw) He—Cd laser at wavelength 441 nm and doubled frequency cw Nd: YAG laser at 532 nm. The spectral energies of these lasers were higher with respect to the energy gaps of the studied crystals. The optical anisotropy was appeared and defected by monitoring of birefringence at probing wavelength of cw He—Ne laser at $\lambda = 3390$ nm. The changes of the laser stimulated near the surface layer morphology was monitored by TEM and AFM methods as well as by the reflected optical second harmonic generation at fundamental wavelength of microsecond CO_2 laser generating at wavelength 10600 nm. This technique may open a new approach for the formation of the near the surface nanolayers in chalcogenides using external cw laser illumination.

1. Introduction

It is well known that chalcogenide materials are promising for application for the laser operated devices due to very high magnitude of photoinduced changes of principal optical constants [1,2]. Particular interest present crystals with heavy cations [3] due to their huge photopolarizability. Another important factor is a significant phonon anharmonicities favoring an occurrence of the laser stimulated effect including the nonlinear optical ones [4–6]. Generally for the chalcogenide materials the photoinduced effects are relatively high which allows to use them for laser operated devices like laser modulators, triggers, deflectors [7,8]. Most of the previous researches were devoted to the studies of crystalline and glass materials [9,10] and there are absent studies devoted to low-dimensional with sizes below 100 nm.

In this work we will explore a possibility to form near the surface states of some ternary chalcogenide crystals using external cw laser light with wavelengths corresponding to higher energies with respect the crystal's gap. Because all the studied crystal are of indirect type their absorption at energies above the energy gap is relatively low (within $10^3 \ldots 10^4$ cm^{-1}). As a consequence the laser beam penetration thickness will be up to 60 nm for the two applied photoinducing lasers: 441 nm and 532 nm. This thickness was independently controlled by absorption spectra of the corresponding rf-sputtered nanofilms. Within this 60 nm nanolayers there occurs an enhanced number of laser induced free carriers forming space gradients of carrier concentration, some photothermal gradients and finally this process leads to enhanced dipole moments. The latter are responsible for the nonlinear optical hyperpolarizabilities Additionally due to laser induced treatment there will occur some changes in the morphology. The photoinduced process will be performed by two split coherent beams formed by the same laser. These beams are incident at different angles on the sample's surfaces [11]. The occurrence of photo-thermal effects will favour additional space thermal gradients of photocarriers. Due to presence of intrinsic cationic defects typical for chalcogenides it is formed additional internal dc-electric field [12]. The existence of such enhanced dipole moments will give additional charge density non-centrosymmetric which usually is responsible for the second order nonlinear optical effects [13] requiring space charge density non-centrosymmetry.

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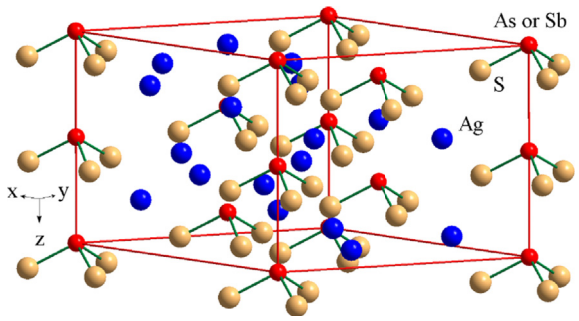

Fig. 1. The package of the anionic groups for the crystals Ag_3AsS_3 or Ag_3SbS_3.

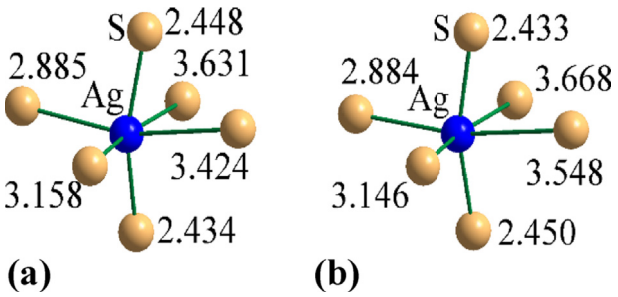

Fig. 2. Inter-atomic distances Ag—S for the crystal Ag_3AsS_3 (a) and Ag_3SbS_3 (b).

In this paper, it will be experimentally demonstrated that varying the photoinduced two beam coherent laser beam wavelengths one can vary the effective laser induced nanolayer's thickness within up to 50 nm. So there occurs a novel opportunity to form the nanolayers without complicated synthesis procedure and using only the appropriate laser beam parameters like power density, polarization, wavelength, space beam profile etc. The origin of the effect is caused by photoinduced polarization of the two coherent beams separated in the space. These beams form some near the surface gratings and partially change morphology [14]. All the laser induced layers demonstrate some relaxation, however generally it does not exceed 22% with respect to the initial laser induced jump. The laser induced surface crystallite have possessed significantly modified structural properties. Moreover, the near the surface state shows some sings of morphological and nanocrystalline changes.

For the studies we have chosen the ternary chalcogenide single crystals Ag_3AsS_3, Ag_3SbS_3, Tl_3SbS_3 [15,16] possessing indirect energy gap with relatively low absorption coefficients. T1 [17, 18]. Additionally occurred birefringence will assist in the fulfilling of phase marching conditions.

Following the reasons presented above we will perform studies of photoinduced changes for the titled chalcogenide crystals under influence of coherent external light generated by cw lasers. We will particularly explore the second order nonlinear optical effects which are sensitive to the charge density acentricity.

2. Experimental

2.1. Materials

The studied Ag_3AsS_3, Ag_3SbS_3, Tl_3SbS_3 crystals were grown by Bridgman method similarly to the described in ref. [19]. Their energy gaps are equal to about 2.085 eV, 1.77 eV and 1.76 eV, respectively. All these energy gaps are of indirect type which means effective contribution of the phonons to fundamental optical absorption. As a consequence for the inter-band optical transitions near the absorption edge there exists a relatively large energy range of low absorption not higher then 10^4 cm^{-1}. The studied samples were cut perpendicularly to the optical trigonal axis in order to avoid the birefringence contribution. Their crystallochemistry structures are depicted in Figs. 1–6.

2.1.1. Ag_3SbS_3 and Ag_3AsS_3

Crystalline structure for both iso-structural crystals Ag_3SbS_3, (pyrargirite) *hR*42, 161 [20] and proustiteAg_3AsS_3, *hR*42, 161 [21] can presented as a packing of atoms of polyhedral SbS_3 or AsS_3 in a form of trigonal piramides as shown in Fig. 1. The silver atoms are situated in the voids between anionic groups with a coordination of deformed octahedra (see Fig. 2). The coordination of anions may be presented as trigonal prism or with addition of 3 additional atoms opposite to particular faces (see Fig. 3). The radiuses of particular atoms exceed the sums of the particular ionic radiuses for the corresponding particular atoms (Ag^+ = 1.14 Å, As^{3-} = 0.69 Å, Sb^{3-} = 0.89 Å, S^{2-} = 1.82 Å [22]).

Following Fig. 2 for the presented structure the silver atoms have an asymmetric coordination with respect to a central atom which is situated between the two sulphur atoms. Moreover, for the structure of the titled compounds the silver atoms have an asymmetric local coordination, where central atom is situated between the two sulphur atoms with shorter bond lengths. The inter-atomic distances for the remaining

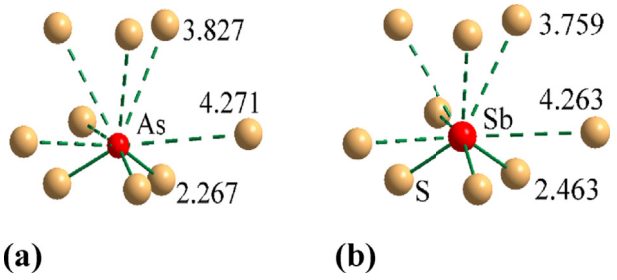

Fig. 3. Inter-atomic distances As—S and Sb—S for crystals Ag_3AsS_3(a) and Ag_3SbS_3(b).

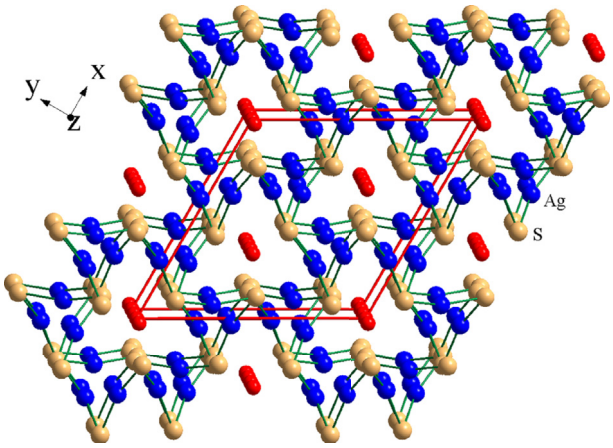

Fig. 4. 3D images of principal inter-chemical bonds Ag—S for crystals Ag_3AsS_3 and Ag_3SbS_3.

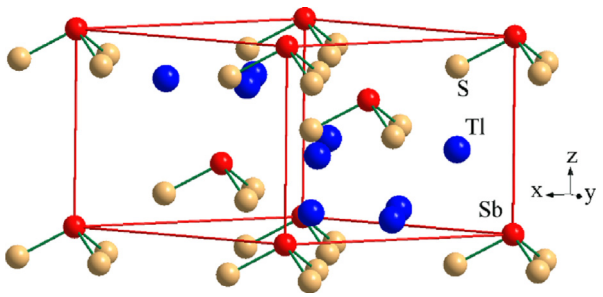

Fig. 5. The package of SbS_3^{3-} ions for single crystal Tl_3SbS_3, *hR*21, 160.