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Electric transport in thin modified films of selenide and sulfide of arsenic

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Abstract. In the studied ChGS the effect of modification influence on the nature of the temperature dependence of conductivity was found. The value of the latter increases with a decrease in the band gap and, accordingly, with an increase of the activation energy. This energy correlates with the change in the height of the potential barrier at the contact between the metal and the chalcogenide glassy semiconductor for different compositions of As_2Se_3 and As_2S_3 materials. The significant role of a single pair of electrons belonging to the atoms of the modifying impurity is noted. The pair of electrons is responsible for the realization of disordered and defective structure and for the formation of the energy system of local states that affect the process of charge carrier transfer.

Keywords: modification, conductivity, activation energy, chalcogenide glassy semiconductor, single pair of electrons

Introduction

An analysis of scientific and technical literature shows that chalcogenide glassy semiconductors are promising materials for use in various fields of science and technology (Chirita, Prilepov 2022). Binary compounds As_2X_3 (X = S, Se) have optical, electrical, and mechanical properties that allow these materials to be used in modern technology, in particular, in telecommunications, medicine, and instrumentation. Amorphous chalcogenide materials are of great interest due to their exceptional structural, electronic and optical properties. Obtaining and studying films based on chalcogenide semiconductors, such as As-Se and As-S, remains an urgent task both from the fundamental and from the applied point of view. Due to this, chalcogenide glassy semiconductors (ChGS) are used in photonics, optoelectronics, micro- and nanoelectronics as devices with optical and electrical memory, media for recording and storing optical and holographic information, in integrated optics, as light guides, etc. (Mehta 2006). ChGS have a number of unique properties that are either partially present or completely absent in crystalline semiconductors: reversible electrical switching and memory effect, photoinduced structural transformations, etc. Also, the advantages of chalcogenide glassy semiconductors include high resistance, a wide glass transition region, and high resistance to moisture. Variation in the composition of ChGS makes it possible to control their properties (optical, thermal, and mechanical). It is known that the structure of ChGS based on arsenic contains structural units such as AsSe, AsS, with homopolar bonds As-As, S-S, Se-Se and heteropolar As-Se, As- S.

Despite the numerous literature data on the study of the structural features, electrical and optical properties of amorphous As_2X_3 (X = Se, S) films, the issues related to the features of the methods for

obtaining amorphous thin films and their influence on the characteristics of the studied films remain unclear (Nguyen et al. 2018). The introduction of metal impurities into the basic grid of the material under study leads to the rearrangement of some chemical bonds and, thus, the appearance of defects, which improves some parameters of the substance. This work presents the results of the study on the influence of the modifier (Pb) on the electrical conductivity of binary compounds of As_2Se_3 and As_2Se_3 ChGS.

Experimental methods

We used the method of formation of ChGS films in vacuum. In this method, thermal deposition, deposition of films in a quasi-closed volume made it possible to achieve the closest approximation to the stoichiometric composition in the vapor phase. The deposition was usually carried out on glass substrates located at a distance of 10–30 cm from the evaporator, depending on the composition of the evaporated material. The substrates were not subjected to forced heating or cooling.

The film was deposited at a rate of 0.1…0.5 μm/min. using conventional thermal evaporation. The thickness of the obtained films was measured using an interferometer and varied within 0.5…5 μm. The conductivity of the modified chalcogenide glass samples at direct current was determined by the leakage current from the time dependence of the absorption current. Immediately before the measurement cycle, the sample was annealed in a cryostat for one hour at T= 420 K.

Results and discussion

Small deviations in the local structure of glass atoms and breaking of chemical bonds can lead to the formation of local (fluctuation) levels in the band gap of a glassy semiconductor, the concentration of which is described by the following formula (Gubanov 1963):

$$N = N_o \frac{4\varepsilon\sqrt{Z}}{2\sqrt{2\pi}} \exp\left(-\frac{2}{\varepsilon^2 Z^2 \varphi^2}\right),$$

where N_o is the number of valence bonds in 1 cm^3, Z is the number of valence bonds in the first coordinate sphere, e is the degree of short-range order violation, ϕ is the coefficient that takes into account the degree to which the wave functions of neighboring atoms overlap.

According to the available measurements of currents limited by the space charge (Zhang, Pantelides 2012), short-range order fluctuations of ChGS (As_2Se_3) create localized levels in the middle of the band gap with a density of 10^{16} cm^{-3} eV^{-1}. The weak effect of impurities on the ChGS conductivity, which is characteristic of arsenic ChGS, was explained according to the ideas of Gubanov–Mott (Kolomiets et al. 1982) by the fact that the glass structure can rearrange around impurity atoms, saturating all chemical bonds. Previously (Kolomiets et al. 1982), it was shown that impurity can effectively affect the electrical properties of ChGS during cold alloying, at which the temperature should not exceed the softening temperature of an amorphous substance. An important point in this case is the choice of the dopant, since in this method of doping the impurity atoms have a much lower possibility for incorporation into the glass atomic framework with the fulfillment of the necessary valence conditions.

Modification of ChGS, i. e., doping with high doses of impurity of a number of transition metals, leads to a sharp increase in conductivity with a relatively slight change in the optical properties of these materials. In this case, an impurity band with the ionization energy depending on the concentration and the type of the modifier is formed in the ChGS band gap (Ghayebloo et al. 2017). The formation of cross-links between molecular chains due to the presence of modifier atoms can lead to an expansion of the band of localized states of the valence band and a corresponding decrease in the band gap. As follows from the experimental data presented in Fig.1 and Fig. 2, temperature dependences of specific conductivity σ of samples As_2Se_3<Pb> and As_2S_3 <Pb> have the form characteristic of most ChGSs and are satisfactorily described by the Arrhenius law (Moynihan et al. 1982):

$$\sigma = \sigma_o \exp\left(-\frac{E_A}{kT}\right),$$

where the pre-exponential factor σ_o is a constant that depends on the properties of the material and is characterized by a single value of the activation energy E_A, T is the absolute temperature.

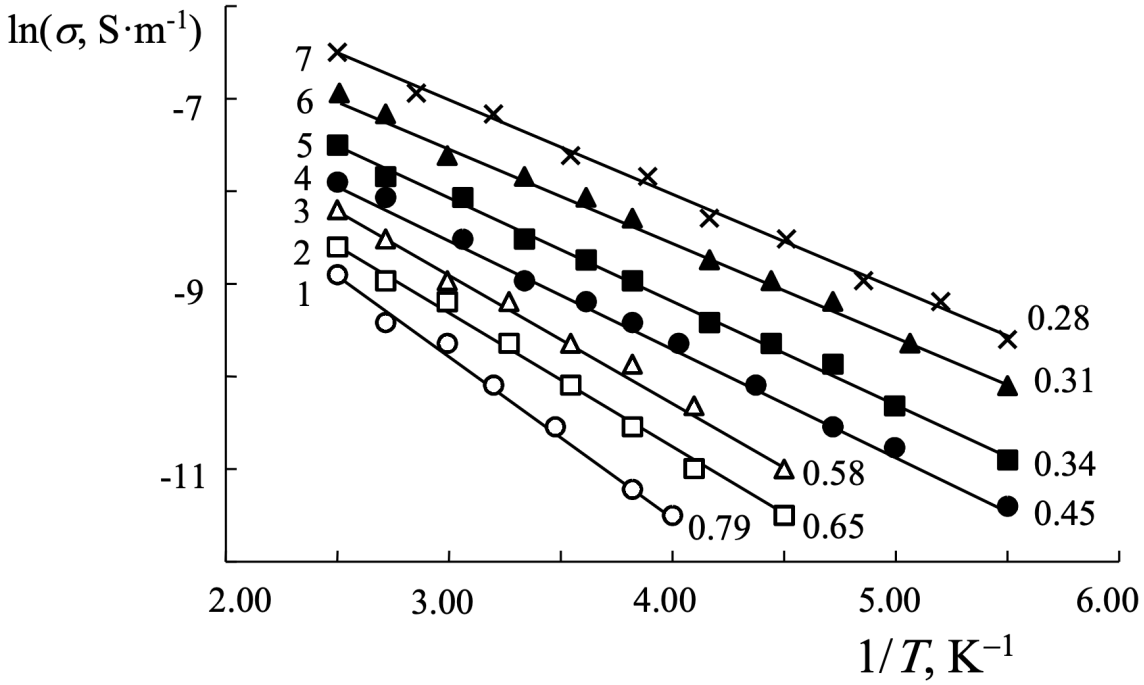

Fig. 1. Temperature dependence of the conductivity of As2Se3 films at different modifier contents:
1—undoped ChGS, 2—1.5, 3—3.2, 4—4.1, 5—6.4, 6—8.3, 7—10.5 at. % Pb.
The values of the activation energy on the dependences are given in eV

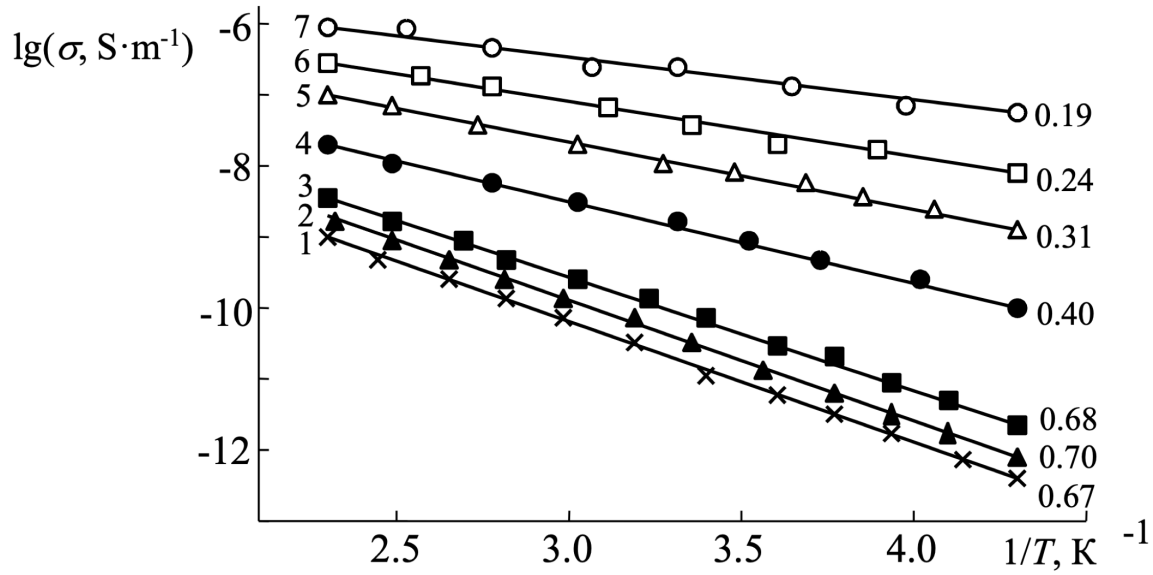

Fig. 2. Temperature dependence of the conductivity of As_2S_3 films at different modifier contents:
1—undoped ChGS, 2—1.3, 3—3.0, 4—4.3, 5—6.2, 6—8.1, 7—9.5 at. % Pb.
The values of the activation energy on the dependences are given in eV

For the modified ChGS films, a larger value of the conductivity increment $\Delta\sigma$ was observed compared to the ChGS of the initial composition. Fig. 3 shows the dependences of the activation energy of the studied samples on the content of the modifying impurity. It follows from the analysis of the obtained results that the parameter σ corresponds to an exponential dependence with a sharply decreasing

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activation energy at small amounts of the introduced modifier from 0.32 to 0.15 eV and a slow decrease in the value of the latter with a further increase in the percentage of the modifier. The observed decrease in the band gap E_g with the introduction of a modifier is apparently due to the fact that some of the Pb atoms embedding in the glass network saturate all their valence bonds and, thereby, form new compounds of the solid solution type. In this case, the parameter E_g is a certain average value between the band gap of arsenic selenide and the band gap of lead selenide, which is a narrower gap semiconductor (Chu, Sher 2007).

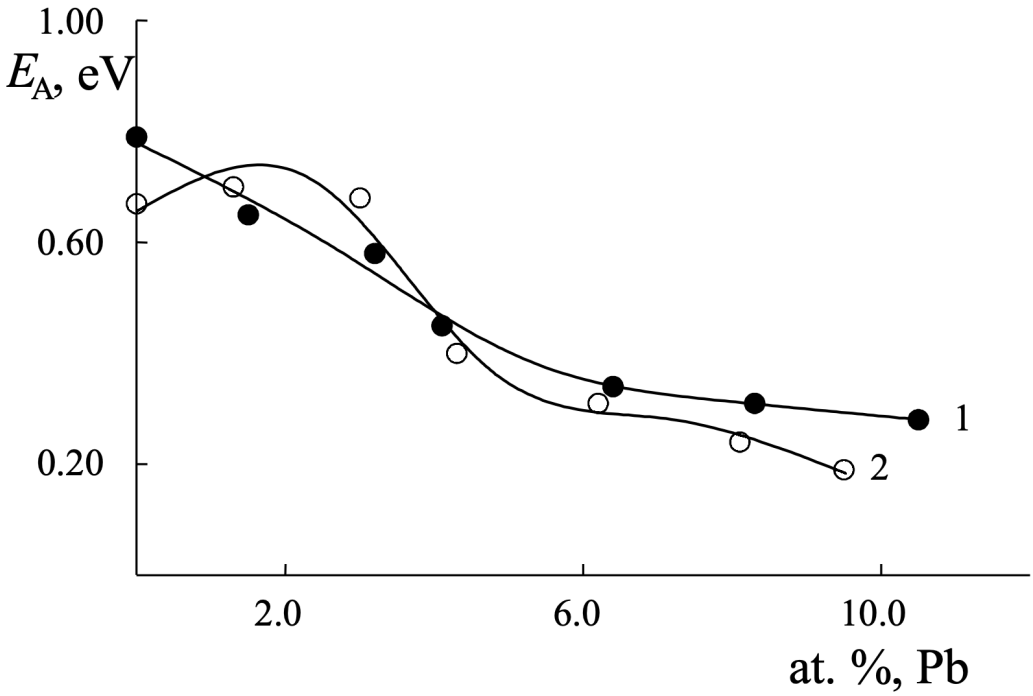

Fig. 3. Dependence of the activation energy of film conductivity As2Se3 (1) and As2S3 (2) on the impurity content

As the results of the experiments performed in the As-Se and As-S systems show, E_A changes little with composition variation but is greater in value for a material with excess sulfur content and less arsenic content with an increase in the amount of selenium. Thus, we can conclude that direct current conductivity is more sensitive to changes in the constant σ_o. At alternating current, both systems retain the dependence of conductivity on composition. Compounds that are close to stoichiometric have a larger E_A value for the As-Se system and a smaller one for As-S. Since there are no pronounced features on the electrical conductivity curves in the studied temperature range, it can be assumed that the Fermi level remains near the middle of the band gap, and the manifestation of the dominant type of conductivity with an increase in the Pb content is due to a change in the ratio of the hole and electron mobilities. We noted the presence of the maximum and minimum values of the parameters σ and E_A depending on the compositional composition of the studied samples, and the introduction of a small percentage (1 ... 1.5%). In the processes of switching and breakdown of ChGS, the field dependence of electrical conductivity plays a decisive role. It follows from the results of numerous previous measurements that ChGSs—in particular, As_2Se_3 and As_2S_3—are quite high-resistant and can be used under conditions of a sufficiently high electric field strength. In the present study, an exponential dependence of the conductivity on the applied field was observed (Figs. 4, 5), which can be interpreted assuming the existence of a current limited by the space charge of a uniform distribution of local states per unit volume in the region of the Fermi level (Zhang, Pantelides 2012).

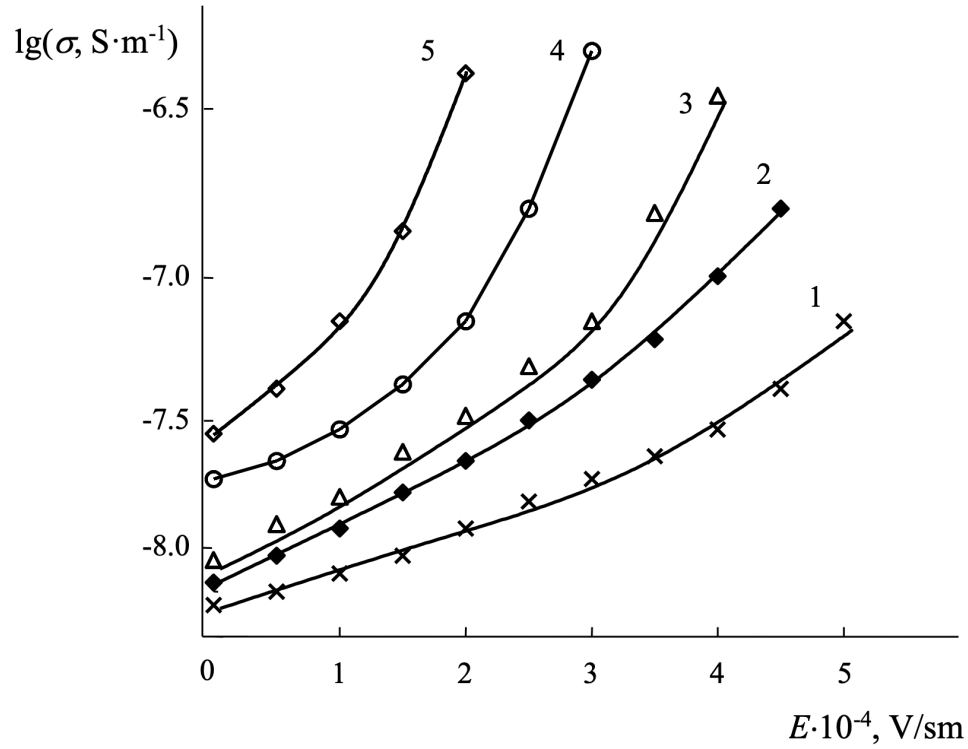

Fig. 4. Field dependence of As_2Se_3 films with different modifier contents: 1—undoped ChGS, 2—1.5, 3—3.2, 4—4.1, 5—6.4 at. % Pb

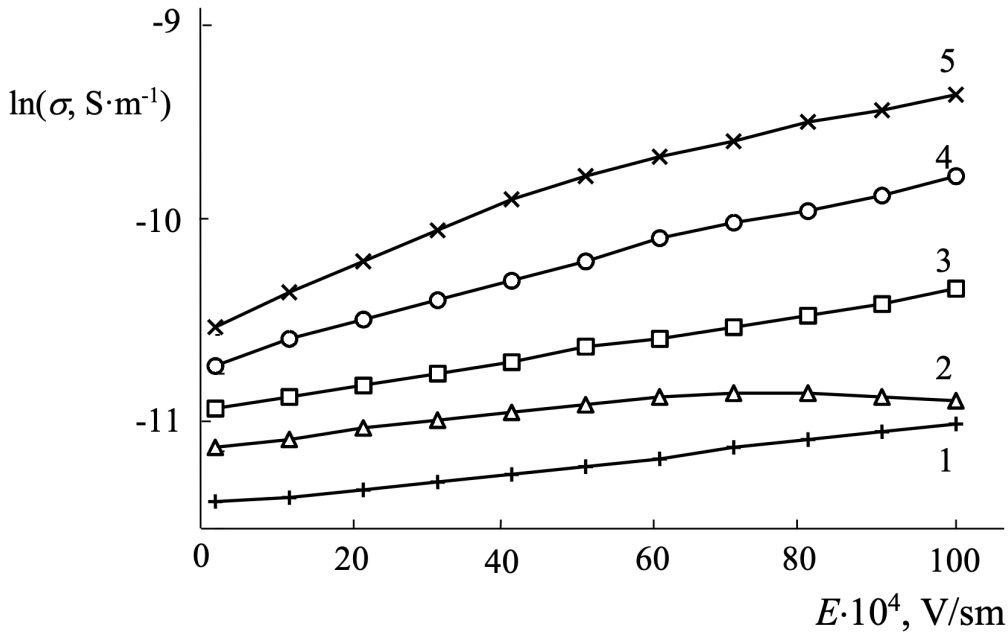

Fig. 5. Field dependence of As_2S_3 films with different contents of the modifier (Pb): 1—undoped ChGS, 2—1.3, 3—3.0, 4—4.3, 5—6.2 at. % Pb

A change in the thickness of the samples has an insignificant effect on the nature of the change in the function $\sigma(E)$ under conditions of constant temperature. Starting from a certain value of the electric field strength ($E_1 < 3 \times 10^{-4}$ V/cm), the obtained characteristics are satisfactorily rectified, answering for most

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samples the dependence $\sigma = \sigma_o \exp(E/E_o)$. With an increase in the electric field strength in the region of $E > 3 \times 10^{-4}$ V/cm, the values of σ increase.

One of the main mechanisms interpreting the nonohmic conductivity in ChGSs (Nardone et al. 2012) assumed that the mobility of localized states depends on the electric field during the transfer of thermally activated charge carriers over multiple barriers.

According to Kazakova and Lebedev, the introduction of a modifier enhances recombination rather than generation processes (Kazakova, Lebedev 1998). Taking into account that holes remain the dominant type of charge carriers, we can assume that the Fermi level E_F shifts to the valence band. This may be due to the fact that some of the modifier atoms form acceptor-type impurity centers. Such a shift in E_F leads to an increase in conductivity and photoconductivity. In ChGS with a high content of Se compared to the stoichiometric composition, the modifier can form a compound (PbSe) without breaking the As-Se bonds. The modifier in this case becomes more stable and less mobile. The formation of the same compound in an As-enriched composition can lead to multiple breaking of the corresponding bonds with the formation of an excessive number of As atoms in the defect structure. Electrically active centers in the band gap of an amorphous semiconductor can be created by atoms of elements that, in addition to orbitals capable of forming strong covalent bonds, also have a set of other orbitals capable of interacting with the orbitals of the surrounding atoms. With a change in the composition of CGS glass, the formation of additional As–As structural bonds, which determine the barrier properties, is also probable.

These elements include bismuth and lead, whose ions (Bi^{3+}) and (Pb^{2+}) have lone electron pair (LEP) of p-electrons on the outer shell of chalcogen atoms whose energy levels fill the top of the valence band. In particular, the energy states of these pairs determine the features of photoinduced processes and switching and memory effects in chalcogenide glasses. LEP affects the shape of molecules and the structure of the crystal lattice, as it has a strong repulsive effect on the neighboring pairs of electrons involved in the bond architecture as well as on other lone pairs. The appearance of the dominant electronic type of conduction is obviously associated with a sharp increase in the mobility of electrons with respect to the mobility of holes. An increase in the mobility of nonequilibrium holes upon modification of As_2Se_3 with bismuth and lead is also evidenced by a decrease in the activation energy of photoconductivity. An analysis of the structural features of the ChGS group under study revealed the essential role of the LEP both in the implementation of the disordered structure and in the formation of the energy structure of local states (Chaudhary et al. 2020). Based on the analysis of the known literature data and comparison of the latter with the experimental results obtained in the course of the study, it can be concluded that defective valence states of the LEP type play a significant role in the process of electric transport.

Conclusions

The temperature dependences of the conductivity of modified As_2Se_3, As_2S_3<Pb> chalcogenide glasses reveal its thermally activated nature. An increase and a sharp decrease in the activation energy with an increase in the level of ChGS modification are associated with the probable formation of solid solutions upon incorporation of modifier (Pb) atoms into the main glass matrix with a simultaneous decrease in the band gap. Compounds that are close to stoichiometric have a larger E_A value for the As-Se system and a smaller one for As-S. An increase in the activation energy of conduction with a change in the composition in the series As_2Se_3...AsSe correlates with the variation in the height of the potential barrier to the metal—the ChGS boundary. There is a field dependence of the conductivity, which can be interpreted within the framework of the current theory, limited by the space charge of a uniform distribution of local states. The results obtained indicate an increase in the proportion of the electronic component of conductivity and suggest the development of additional mechanisms of electrical transport. The study of amorphous compounds of the modified ChGS type encounters fundamental difficulties due to the difficulty of obtaining samples of a stable and accurate composition due to their tendency to form structures, the disordering of which is largely due to the presence of LEP.

The experimental studies carried out in this work make it possible, to a certain extent, to fill some gap in the study of ChGS electrical properties as well as to expand the scope of their practical application as base materials for electronics with improved performance.

Conflict of Interest

The author declares that there is no conflict of interest, either existing or potential.

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