MICROSTRUCTURE AND MECHANICAL PROPERTIES OF TERNARY FLAKY SEMICONDUCTING COMPOUNDS

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Abstract

Multicomponent sulfides $ZnIn_2S_4$, $Zn_3In_2S_6$, and $CoGaInS_4$ were obtained, and their mechanical properties (microhardness, plasticity, and brittleness) were studied. It was shown that the deformation peculiarities of the investigated compounds are connected with the specific layered crystalline structure.

1. Introduction

Ternary flaky semiconducting compounds are a promising material for the modern micro- and optoelectronics [1-4]. New multicomponent sulfides, such as three-packet $ZnIn_2S_4$ and single-packet $Zn_3In_2S_6$ crystal polytypes, as well as the $CoGaInS_4$ compound, are typical representatives of this class of crystals. Various devices have been elaborated on their basis. The compounds of the $Zn_xIn_2S_{3+x}$ type show high photosensitivity and intensive luminescence and can be used as effective ultraviolet detectors, solar cells, etc. The $CoGaInS_4$ crystals are of interest due to application as antiferromagnetic materials [2-5].

For the successful utilization of these materials, it is necessary to know their mechanical properties. Some features of plastic deformation observed using the microindentation and scratching methods are presented in this work.

2. Experimental

The compounds were obtained from the vapor phase by the method proposed earlier [5]. This technique makes it possible to grow the crystals in the form of thin hexagonal layered plates with dimensions of ~(20 × 12 × 0.8) mm^3. Single crystals were confined by the (0001) and (0110) faces. Atom coordinates and structure parameters are in accordance with the results reported in [6, 7].

The thin grown steps can be seen under optical and electron microscopic investigations of all studied ternary semiconductor compounds. At the same time, the growing features of hexagons were sometimes noticed on the as-grown surface of the $Zn_xIn_2S_{3+x}$ samples (Fig. 1). These hexagons probably begin to form from the helicoidal dislocations existing in the crystal volume and outgoing on the growth surface and build up a new growth layer of the crystal structure. Structurally perfect single crystals have a low dislocation density ($N_d = 10^2$, cm^{-2}) and are superior to the ZnS crystals in stability [8]; it was also observed that ternary flaky semiconducting compounds exhibit specific mechanical properties [4].

A PMT-3 microhardness tester supplied with a rotating device was used for the crystal deformation and for the determination of microhardness via penetration (H_V) and sclerometric (H_S) methods. A Vickers' diamond pyramid was used for these experiments. The load (P) applied to the indenter was varied between 0.01 and 0.5 *N*. The hardness values were determined using the standard formulae [9]. A device for registration of acoustic emission (AE) signals was applied for the determination of crystal brittleness.

Fig. 1. As-grown hexagons on the $ZnIn_2S_4$ (0001) plane.

3. Results and Discussion

One of the unusual mechanical properties of the investigated flaky compounds is the inconstant microhardness values. They are dependent on the load applied to the indenter, and the *H(P)* dependences exhibit a nonmonotonous behavior. The microhardness increases in the range from low to middle loads (0.03÷0.2*N*). Here the microhardness values change in the intervals between 0.2÷0.5 *GPa*, 0.25÷0.5 *GPa*, and 0.17÷0.3 G*Pa* for $ZnIn_2S_4$, $Zn_3In_2S_6$, and $CoGaInS_4$, respectively. The microhardness reaches its maximal values at definite loads and then begins to decrease with a further increase in load. It was observed that the critical load value for the maximal *H* depends on the sample thickness (*h*). The microhardness values begin to decrease if the deformation depth reaches approximately one-half the sample thickness (0.5*h*). After that, the H_V values begin to diminish.

In order to understand the above behavior of the microhardness vs. load dependence, it is necessary to investigate the surface relief in the indentation neighborhood via varying the load.

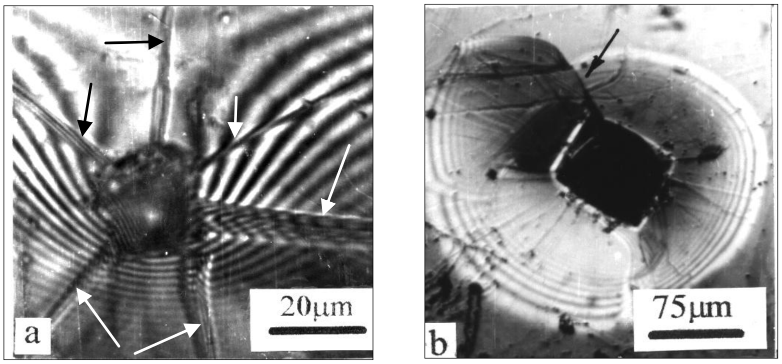

Fig. 2. $ZnIn_2S_4$ crystal, plane (0001): (a) interference around indentation. $P = 0.3N$; (b) circle-like deformation near by indentation. P=0.2*N*. (Twins are marked by arrows).

It was noticed that the surface is essentially modified near the indentations (Fig. 2) and scratches: the crystal exhibits a tendency to the local lowering of the surface which increases while approaching the indentations or the scratches. The lowering is intensified with load increase, too. So, the indentations obtained at $P>0.1$ *N* look in interference regime as situated in a pit (Fig. 2a).

The elastoplastic local flexure of the crystals under heavy loads on the indenter is so deep that conical hills of the forced out materials can be seen on the opposite side of the specimen. This is very well observed in the form of the concentric rings in the interference regime (Fig. 3). Sometimes the spontaneous (natural) interference generated by the crystal lamination at the indenter penetration is observed around the indentations (Fig. 2b). In some cases, the material lamination is accompanied by the appearance of twins (marked by arrows in Fig. 2).

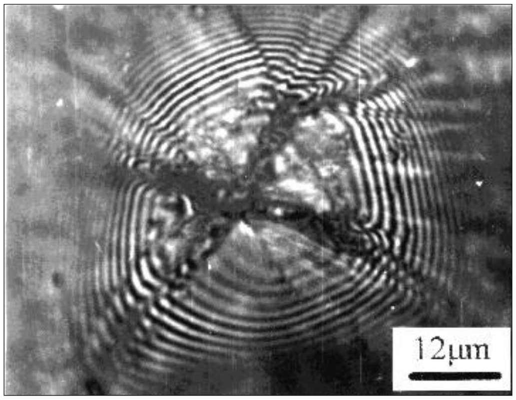

Fig. 3. Conical hill of the forced out material on the opposite side of the deformed $Zn_3In_2S_6$ crystal in the interference regime; (0001) plane; $P = 0.5N$.

It was established that the contribution of the twinning mechanism in microindentation process increases with increasing load (cf. Figs. 2b and 2a). A similar deformation has been previously found on the (111) plane of the bismuth type semimetals, which possess layer-like structure [9]. At the same time, unlike semimetals, the frail mechanism takes part in the deformation of ternary flaky compounds side by side with twinning one. However, the fragile destruction of the materials arises only in a thin superficial layer (~0.4% of the thickness of the deformed zone). This result indicates a good quality of crystals and their high strength properties.

The microstructure investigation showed that the tendency to twinning mechanism is more pronounced for $Zn_xIn_2S_{3+x}$ crystals. Tendency of the flaky compounds to twinning and frail destruction was also studied by (AE) method (table).

AE signals appearing under indentation. (N_1 and N_2 are the number of signals registered at the loading and unloading stages, respectively)

Crystal	*P, N*	N_1	N_2	$\Delta N = N_1 - N_2$
$CoGaInS_4$	0.1	700	2600	1900
	0.2	1180	4200	3020
$Zn_3In_2S_6$	0.1	430	1800	1370
	0.2	440	2180	1740

It is evident from the table that deformation of the $CoGaInS_4$ crystals is accompanied by the appearance of a greater number of signals than in the case of $Zn_3In_2S_6$. This indicates the smaller destruction of $Zn_3In_2S_6$ crystals as compared with $CoGaInS_4$ ones. Also, one can see that both the fragile destruction and twinning processes play a greater role when the crystals are unloaded, i.e., during crystal relaxation.

Thus, the results of the investigation of microstructure and mechanical properties of $Zn_xIn_2S_{3+x}$ and $CoGaInS_4$ indicate some specific peculiarities of their deformation. It was noticed that several mechanisms of deformation of flaky ternary compounds take place under the action of a concentrated load on the (0001) plane. They are: bending of crystal layers in the C-axis direction; plastic deformation by the twinning mechanism, brittle-plastic deformation of indentation and scratch surface with the formation of a nanostructural modification of the material in the contact zone and with the generation of thin cracks out of the contact region.

The existence of the nanostructure in the contact zone was observed under studying a very thin superficial layer after deformation. Just below it, mainly plastic indentations and scratches appear; this can be associated with either a local plastic compaction of the structure layers or a contribution of dislocation deformation mechanism.

4. Conclusion

The good-quality single crystals of the $Zn_xIn_2S_{3+x}$ and $CoGaInS_4$ ternary flaky semiconductor compounds were obtained. The strength and plastic properties of these crystals were studied, and the main mechanisms of deformation under the action of a concentrated load were proposed. It was shown that the specific deformation of multinary compounds takes place due to their stratified crystalline structure.

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